Intensity Statistics and Direct Methods for Incommensurately Modulated Crystals and Misfit Layer Compounds

Erwin J. W. Lam

Intensity Statistics and Direct Methods for Incommensurately Modulated Crystals and Misfit Layer Compounds

This thesis was typeset using LaTeX.
The program *DVIPS*, by Radical Eye Software, was used to include the postscript figures.

Intensity Statistics and Direct Methods for Incommensurately Modulated Crystals and Misfit Layer Compounds

Een wetenschappelijke proeve op het gebied van de
Natuurwetenschappen

Proefschrift

ter verkrijging van de graad van doctor
aan de Katholieke Universiteit Nijmegen,
volgens besluit van het College van Decanen
in het openbaar te verdedigen op
dinsdag 29 november 1994,
des namiddags te 1.30 uur precies

door

Erwin Jacobus Wilhelmus Lam
geboren op 10 september 1960 te Hilversum

Promotores: Prof. Dr. P. T. Beurskens
Prof. Dr. A. G. M. Janner
Copromotor: Dr. S. van Smaalen (Rijksuniversiteit Groningen)

Het in dit proefschrift beschreven onderzoek werd uitgevoerd onder auspicien van de stichting *Scheikundig Onderzoek Nederland* (SON) met financiele steun van de *Nederlandse Organisatie voor Wetenschappelijk Onderzoek* (NWO)

Lam, Erwin Jacobus Wilhelmus
Thesis, University of Nijmegen, Department of General and Inorganic Chemistry, Research Group Crystallography, 1994
ISBN 90–9007556–9
Realisatie Universitair Publikatiebureau KUN
Omslagtekening *'Het kristalmannetje'*, met toestemming van O Kerssen

Aan mijn ouders

Bij deze wil ik graag iedereen bedanken die op enigerlei wijze heeft bijgedragen aan de totstandkoming van dit proefschrift. In de eerste plaats denk ik hierbij aan mijn promotores Prof. Beurskens en Prof. Janner en mijn copromotor Dr. van Smaalen die mij bij het uitvoeren van dit onderzoek altijd enthousiast gesteund hebben met ideëen en adviezen. (Mijn vele reizen naar Groningen hebben duidelijk hun nut gehad.)

In particular, I would like to express my gratitude to Professor Fan Hai-Fu (Chinese Academy of Sciences, Beijing) for a very fruitfull cooperation. A discussion with Professor Fan, during the summerschool in Erice, Italy (1990), inspired me regarding the investigation of normalized structure factors for incommensurately modulated crystals. In the autumn of 1992, Professor Fan visited our laboratory (sponsored by the RIM) where we started working on direct methods for incommensurate intergrowth compounds. I also would like to thank Dr. Hao Quan, who is a former student of Professor Fan and who visited us during the summer of 1989. Dr. Hao taught me a lot about direct methods for incommensurately modulated crystals.

Further, I would like to express my gratitude to Dr. Petříček (Academy of Sciences of the Czech Republic) for making available The Computing System *JANA*.

Tevens wil ik alle (ex)medewerkers van de afdeling Kristallografie van de Katholieke Universiteit Nijmegen bedanken voor de prettige samenwerking. In het bijzonder gaat mijn dank uit naar mijn kamergenoot Wil (*koffiiiiiiiieeeeeeee*) Bosman voor de nodige ondersteuning op computergebied en naar Jan Smits voor de metingen aan (peryleen)$Co(mnt)_2(CH_2Cl_2)_{0.5}$ en het vele proeflezen. De beide mooi-weer-wandelaars, Randy Israël en René de Gelder, bedank ik voor het vele programmeerwerk dat ze mij uit handen genomen hebben. Dat René leuk kan tekenen blijkt wel uit de tekening achter in het proefschrift. De secretaresses Riet Oerlemans, Eva Schaepkens en Hanny Schuurs worden bedankt voor al die werkzaamheden die zoveel tijd kosten als je ze zelf moet doen.

Mevrouw Vos (Theoretische Fysica I) wordt eveneens bedankt voor het verrichten van enig type-werk.

Dr. Schutte (Rijksuniversiteit Groningen) was zo vriendelijk om mij gedurende de eerste maanden van het onderzoek wegwijs te maken in het gebruik van het computerprogramma *REMOS*.

Verder wil ik hier nog de vakgenoten uit Groningen, Delft en Nijmegen bedanken vanwege de nuttige bijeenkomsten van de werkgroep 'Incommensurabel'.

Manuscriptcommissie: Dr. R. de Gelder
Dr. R. Peschar (Universiteit van Amsterdam)

Contents

1

General Introduction

Today, direct methods are being used extensively to determine the structures of three-dimensionally periodic crystals from their measured X-ray diffraction intensities. This thesis describes research aimed at extending direct-methods procedures towards structure determination for aperiodic crystals. In section 1.1, a summary is given of X-ray diffraction* and statistical methods for X-ray crystal-structure analysis as applied to conventional crystals. Many of the symbols used in this thesis are hereby introduced. In section 1.2, incommensurate order in crystals is introduced. The scope of this thesis is defined in the last section of this introduction.

1.1 Conventional X-ray crystal-structure analysis

X-ray diffraction

A crystal is usually described in terms of a building block (unit cell) which is repeated *ad infinitum* on a three-dimensional periodic lattice (the direct lattice). In general, the unit cell has the form of a parallelepiped. The basic vectors of the direct lattice are identical to the vectors $\mathbf{a}_i$ $(i = 1, 2, 3)$ which span the unit cell. All lattice vectors $(\mathbf{L})$ can be written as

$$\mathbf{L} = \sum_{i=1}^{3} l_i \, \mathbf{a}_i, \tag{1.1}$$

where the numbers l_i $(i = 1, 2, 3)$ are integers. The electron density (ρ) of the crystal shows the same three-dimensional periodicity as the underlying direct lattice:

$$\rho(\mathbf{r} + \mathbf{L}) = \rho(\mathbf{r}), \tag{1.2}$$

where $\mathbf{r}$ is an arbitrary position in the unit cell.

X-rays incident upon a crystal will be scattered by the electrons. The diffraction vector $\mathbf{H}$, which is the difference between the wave vector of the diffracted X-ray beam and the wave vector of the incident X-ray beam, can be written in terms of the reciprocal-lattice vectors $\mathbf{a}_i^*$ $(i = 1, 2, 3)$ as

$$\mathbf{H} = \sum_{i=1}^{3} h_i \, \mathbf{a}_i^*. \tag{1.3}$$

The reciprocal-lattice vectors are defined through the relation $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$, where $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. Three-dimensional translational symmetry implies that

*An introduction to X-ray diffraction for conventional crystals and aperiodic crystals can be found in chapter 3 of Giacovazzo *et al.* (1992) and references therein.

diffracted intensity is only found in directions that correspond to the nodes of the reciprocal lattices, *i.e.* the components of the diffraction vector [(1.3)] must be integers.

Thus, X-ray diffraction data consists of intensities I, one value for each diffraction vector $\mathbf{H}$. The intensities depend on the electron density in the crystal through the amplitude $|F|$ of the structure factor as

$$K^2 I(\mathbf{H}) = |F(\mathbf{H})|^2, \tag{1.4}$$

where K is the scale factor which reflects the fact that measured intensities are on a relative scale whereas $|F(\mathbf{H})|$ is on an absolute scale. The structure factor $F(\mathbf{H})$ for X-ray diffraction is defined as the three-dimensional Fourier transform of the electron density in the unit cell:

$$F(\mathbf{H}) = \int_V \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{1.5}$$

Here, the integral extends over the volume V of the unit cell. The inverse transformation of (1.5) gives the electron density as a three-dimensional Fourier summation over the integer components of all diffraction vectors in reciprocal space:

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}). \tag{1.6}$$

In good approximation, the electron density of a crystal can be written as the sum of the contributions from the individual atoms. For the electron density in one unit cell, this is:

$$\rho(\mathbf{r}) = \sum_{\mu=1}^{N} \rho_\mu(\mathbf{r} - \mathbf{r}^\mu). \tag{1.7}$$

Here, ρ_μ is the electron density of atom μ at the origin and $\mathbf{r}^\mu$ is the position of this atom. The summation extends over all atoms (N) in the unit cell. The atomic form factor f^μ, which expresses the scattering from a single atom μ at the origin, can be obtained in a way similar to (1.5) as

$$f^\mu(\mathbf{H}) = \int \rho_\mu(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r})\, \mathrm{d}\mathbf{r}, \tag{1.8}$$

where the integral now extends over the entire atomic domain in physical space. With (1.7), the structure factor [(1.5)] can be written as

$$F(\mathbf{H}) = \sum_{\mu=1}^{N} f^\mu(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}^\mu). \tag{1.9}$$

If it is further assumed that atoms are spherical and that the thermal vibration of an atom is isotropic, the atomic form factor can be approximated by

$$f^\mu(\mathbf{H}) = f_0^\mu(s) \exp(-B^\mu s^2), \tag{1.10}$$

where f_0^μ is the form factor for atoms at rest, B^μ is the isotropic temperature parameter and $s = (\sin\theta)/\lambda = |\mathbf{H}|/2$. Here, θ is half the scattering angle of the diffracted X-ray beam, λ is the wavelength of the X-ray radiation and $|\mathbf{H}|$ is the length of the diffraction vector $\mathbf{H}$.

The purpose of a crystal-structure analysis is to find the positions of the atoms in the crystal. Once these are known, many features of the molecular conformation (such as bond distances and bond angles) can be calculated. The atoms in the crystal can be localized by searching for the maxima in the electron-density function [(1.7)] which, in turn, can be obtained as a three-dimensional Fourier synthesis [(1.6)] of the set of structure factors, if they were known. In general, however, a structure factor is a complex number,

$$F(\mathbf{H}) = |F(\mathbf{H})| \exp[i\varphi(\mathbf{H})], \tag{1.11}$$

with amplitude $|F(\mathbf{H})|$ and phase $\varphi(\mathbf{H})$, but from (1.4), it follows that the X-ray diffraction intensities only give information about the structure-factor amplitudes. Although information about the phases of the structure factors is implicitly included in the collected diffraction intensities, this phase information is not available in a direct way.† Therefore, it is impossible to obtain the electron density of the crystal by a straightforward three-dimensional Fourier synthesis [(1.6)] of the set of structure factors. This problem is known as the phase problem in X-ray crystallography.

Many techniques to overcome the phase problem have been developed during the past decades. Well known examples of these techniques are 'trial and error', Patterson methods, isomorphous replacement and direct methods. This thesis will only be concerned with direct methods which employ statistical relations between the phases of the structure factors. A short review of the most important tools of direct methods will be given below.

Intensity Statistics

One of the first results of the application of statistics to X-ray diffraction data is concerned with estimating the average X-ray diffraction intensity (Wilson, 1942). Here, it is assumed that atoms are randomly distributed throughout the unit cell. With the electron

†For each diffraction vector $\mathbf{H}$, there exists an equation which relates the measured X-ray diffraction intensity $I(\mathbf{H})$ to the unknown structural parameters. [Here, for example, this equation could be a combination of expressions (1.4) and (1.9).] In general, the number of reflections that has been measured will be much larger than the number of structural parameters, which results in a system of independent equations that is overdetermined. This means that the structural parameters can be determined from the diffraction data and, consequently, the measured intensities must contain information about the phases of the structure factors.

density written as the sum of contributions from the individual atoms [(1.7)], a theoretical expression for the expectation value of $|F(\mathbf{H})|^2$ can be derived from (1.9) as

$$\left\langle |F(\mathbf{H})|^2 \right\rangle_s = \exp(-2Bs^2) \sum_{\mu=1}^{N} [f_0^\mu(s)]^2. \tag{1.12}$$

The average $\langle \cdots \rangle_s$ is taken over a sufficiently large set of reflections having s within a given small interval. The right-hand side of expression (1.12) is a function of s. Furthermore, expression (1.12) only depends on the overall isotropic temperature parameter B, which replaces the isotropic temperature parameters B^μ of the individual atoms, and the contents of the unit cell.

Because the absolute scale of the measured diffraction data is not known, expression (1.12) is combined with expression (1.4) to give the so called Wilson plot:

$$\ln \left\{ \langle I(\mathbf{H}) \rangle_s \Big/ \sum_{\mu=1}^{N} [f_0^\mu(s)]^2 \right\} = -2 \ln K - 2Bs^2. \tag{1.13}$$

For a given set of diffraction intensities, the left-hand side of (1.13) can be obtained by calculating the average of $I(\mathbf{H})$ over all reflections having s within a given small interval. The right-hand side of (1.13) is a linear function of s^2 and can be employed by a least-squares fitting procedure to estimate the scale factor K and the overall isotropic temperature parameter B.

Note that the expectation value $\langle I(\mathbf{H}) \rangle_s$ really is a statistical property of the diffracted intensities. One may expect the values of the individual averages to deviate from the expectation value, as is confirmed by experiment.

Normalized structure factors E, which are frequently used in direct-methods procedures to estimate the 'importance' of reflections with respect to the reliability of phase relations, can be defined according to

$$E \equiv F \left\langle |F|^2 \right\rangle^{-1/2} \tag{1.14}$$

with $\langle |F|^2 \rangle$ usually given by (1.12). In a statistical sense, normalized structure factors are independent of the shapes of the atoms (this includes thermal vibration). For this reason, normalized structure factors are associated with crystals consisting of nonvibrating point atoms. One important characteristic of normalized structure factors is that, according to definition (1.14), $\langle |E|^2 \rangle = 1$, independent of the set of reflections for which the average is calculated and independent of the contents of the unit cell.

Another result of the application of statistics in X-ray crystallography is the derivation of distribution functions for X-ray diffraction intensities. Wilson (1949) showed that, for

crystals with many atoms randomly distributed throughout the unit cell, the central-limit theorem can be used to obtain the probability distribution of the diffracted intensities. Distribution functions $P_{|E|}$ for normalized structure-factor amplitudes can be derived in a similar way (Ramachandran & Srinivasan, 1959; Giacovazzo, 1980). For noncentrosymmetric crystals

$$P_{|E|}(x) = 2x \exp(-x^2) \tag{1.15}$$

and for centrosymmetric crystals

$$P_{|E|}(x) = (2/\pi)^{1/2} \exp(-x^2/2), \tag{1.16}$$

where $P_{|E|}(x)\,\mathrm{d}x$ is the probability for the value of $|E|$ to lie between x and $x+\mathrm{d}x$. Because of the nature of the central-limit theorem, expressions (1.15) and (1.16) are approximations, valid only in the limiting case of a large number of atoms in the unit cell. In practice, deviation from the theoretical distributions occurs when the atoms are not randomly distributed throughout the unit cell, *e.g.* when atoms occupy special positions or when pseudo translations exist in the structure (superstructure effects).

Direct methods

Consider a crystal with well separated atoms (atomicity) in the unit cell, *i.e.* the atomic electron densities (ρ_μ) do not overlap. The 'squared' structure, with electron density

$$\begin{aligned} \rho^{\mathrm{sq}}(\mathbf{r}) &\equiv \rho^2(\mathbf{r}) \\ &= \sum_{\mu=1}^{N} \rho_\mu^2(\mathbf{r} - \mathbf{r}^\mu) \end{aligned} \tag{1.17}$$

in the unit cell, will also have well resolved atoms at exactly the same positions as the atoms in the original structure [(1.7)], although the peaks in the squared electron-density function will be higher and smaller. It is therefore obvious that, in case of equal atoms and for a given diffraction vector $\mathbf{H}$, the structure factor F^{sq} of the squared structure is proportional to the structure factor F of the original structure. On the other hand, it follows from Fourier theory that the Fourier transform of a product of two functions is equal to the convolution of the Fourier transforms of the these functions. Thus, with the structure factor being a function in reciprocal space, it follows that F^{sq} is identical to the autoconvolution of the structure factors F of the original structure. This leads to the following relation between structure factors (Sayre, 1952):

$$F(\mathbf{H}) = \Theta(|\mathbf{H}|) \sum_{\mathbf{H}'} F(\mathbf{H}')F(\mathbf{H} - \mathbf{H}'). \tag{1.18}$$

For a given diffraction vector $\mathbf{H}$, $\Theta(\mathbf{H})$ is a positive real number. Consequently, the phase of the structure factor $F(\mathbf{H})$ is equal to the phase of the summation on the right-hand side of (1.18). This means that relation (1.18) can be used to calculate the phase $\varphi(\mathbf{H})$ of structure factor $F(\mathbf{H})$ from the phases of other structure factors, without precise knowledge of $\Theta(|\mathbf{H}|)$. However, the Sayre equation [(1.18)] is not very suitable for use in *ab initio* direct methods. The problem is that, although the summation with respect to $\mathbf{H}'$ converges, it is in principle an infinite summation over all nodes of the reciprocal lattice. This means that, in order to determine the phase $\varphi(\mathbf{H})$, a large number of other phases must be known in advance, which is usually not the case. Furthermore, most of the terms in the summation have small amplitudes and completely different phases. A summation over a limited number of these terms may then result in an unreliable estimate of the phase $\varphi(\mathbf{H})$. Hence, in practice, a reliable estimate of the phase $\varphi(\mathbf{H})$ by use of (1.18) is not possible.

Sometimes, however, the Sayre equation may be dominated by a single term in the summation. This occurs when $|F(\mathbf{H})|$ is large and when, for some term in the summation, $|F(\mathbf{H}')F(\mathbf{H}-\mathbf{H}')|$ is much larger than for the other terms. Then, the phase $\varphi(\mathbf{H})$ is very likely to be close to $\varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}')$.

As explained above, the Sayre equation is based on atomicity. When, in addition, atoms are randomly distributed throughout the unit cell, it becomes possible to derive more explicit relations between a limited number of structure-factor phases. This probabilistic approach leads, for example, to the triplet-phase relation which, for noncentrosymmetric crystals, can be written as

$$\varphi(\mathbf{H}) \approx \varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}'). \tag{1.19}$$

Here, the $\approx$ sign means 'probably close to'. The probability distribution for the true value of $\varphi(\mathbf{H})$ being equal to ϕ is (Cochran, 1955)

$$P_\varphi(\phi) = \frac{1}{2\pi I_0[\kappa(\mathbf{H},\mathbf{H}')]} \exp\{\kappa(\mathbf{H},\mathbf{H}')\cos[\phi - \varphi(\mathbf{H}') - \varphi(\mathbf{H}-\mathbf{H}')]\}, \tag{1.20}$$

where I_0 is a modified Bessel function of the first kind and

$$\kappa(\mathbf{H},\mathbf{H}') = 2C|E(\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')| \tag{1.21}$$

with

$$C = \frac{\sum_{\mu=1}^{N} Z_\mu^3}{\left(\sum_{\mu=1}^{N} Z_\mu^2\right)^{3/2}} \tag{1.22}$$

$$= N^{-1/2} \qquad \text{(for equal atoms)}. \tag{1.23}$$

Here, Z_μ is the atomic number of atom μ. The distribution function (1.20) has a peak at $\phi = \varphi(\mathbf{H}') + \varphi(\mathbf{H} - \mathbf{H}')$. When the value for κ increases, the width of this peak will become narrower and, consequently, estimate (1.19) for $\varphi(\mathbf{H})$ will become more reliable. This can be used to estimate $\varphi(\mathbf{H})$, once the amplitudes $|E(\mathbf{H})|$, $|E(\mathbf{H}')|$ and $|E(\mathbf{H}-\mathbf{H}')|$, as well as the phases $\varphi(\mathbf{H}')$ and $\varphi(\mathbf{H} - \mathbf{H}')$ are known.

As indicated by the Sayre equation [(1.18)], there are infinitely many triplet-phase relations that estimate the phase $\varphi(\mathbf{H})$, all with a different reliability. However, in practice, only a limited number of relations is considered. In that case, one usually employs the tangent formula which can be considered as a 'weighted average' over a limited set of triplet-phase relations. For noncentrosymmetric structures, the tangent formula can be written as

$$\tan(\beta) = \frac{\sum_{j=1}^{r} \kappa(\mathbf{H}, \mathbf{H}'_j) \sin[\varphi(\mathbf{H}'_j) + \varphi(\mathbf{H} - \mathbf{H}'_j)]}{\sum_{j=1}^{r} \kappa(\mathbf{H}, \mathbf{H}'_j) \cos[\varphi(\mathbf{H}'_j) + \varphi(\mathbf{H} - \mathbf{H}'_j)]}, \tag{1.24}$$

where β is the estimated value for $\varphi(\mathbf{H})$ and the summation with respect to j counts the number (r) of triplet-phase relations participating in this estimate. The probability distribution for the true value of $\varphi(\mathbf{H})$ being equal to ϕ is now given by

$$P_\varphi(\phi) = \frac{1}{2\pi I_0(\alpha)} \exp\{\alpha \cos[\phi - \beta]\}. \tag{1.25}$$

When the nominator and denominator of (1.24) are denoted $T(\mathbf{H})$ and $B(\mathbf{H})$, respectively, α can be obtained from

$$\alpha^2 = T^2(\mathbf{H}) + B^2(\mathbf{H}). \tag{1.26}$$

Note that probability distribution (1.25) for the tangent formula is basically of the same form as probability distribution (1.20) for a single triplet-phase relation, with α having the same meaning as κ. Consequently, the estimate $\varphi(\mathbf{H}) \approx \beta$ will be more reliable for larger values of α.

For centrosymmetric structures, where structure-factor phases can only assume the values 0 or π, similar equations can be derived. The triplet-phase relation now becomes a sign relation (Cochran & Woolfson, 1955),

$$\text{sign}[E(\mathbf{H})] \simeq \text{sign}[E(\mathbf{H}')E(\mathbf{H} - \mathbf{H}')]. \tag{1.27}$$

Here, the $\simeq$ sign means 'probably equal to'. The probability that sign relation (1.27) is correct is given by

$$P^+ = \frac{1}{2} + \frac{1}{2} \tanh[x(\mathbf{H}, \mathbf{H}')] \qquad (x = \kappa/2), \tag{1.28}$$

where κ is defined by (1.21). As for noncentrosymmetric structures, expression (1.28) indicates that relation (1.27) becomes more reliable with increasing κ. For centrosymmetric structures, the tangent formula [(1.24)] reduces to

$$\text{sign}[E(\mathbf{H})] \simeq \text{sign}\left[\sum_{j=1}^{r} E(\mathbf{H}'_j)E(\mathbf{H}-\mathbf{H}'_j)\right]. \tag{1.29}$$

The probability that relation (1.29) is correct is given by

$$P^+ = \frac{1}{2} + \frac{1}{2}\tanh\left[\left|\sum_{j=1}^{r} x(\mathbf{H},\mathbf{H}'_j)\right|\right], \tag{1.30}$$

which is basically the same function as (1.28). Thus, relation (1.29) will be more reliable for increasing $|\sum_{j=1}^{r} x(\mathbf{H},\mathbf{H}'_j)|$.

In order to use the probability relations (1.19), (1.24), (1.27) and/or (1.29) in direct methods, some starting phases must be known in advance. Some of the phases can be assigned a value in order to fix the origin and the enanthiomorph. These values may be chosen arbitrarily. Other phases can be assigned a symbol. Various symbolic-addition procedures (Beurskens, 1963, 1964; Karle & Karle, 1966) can then be used to obtain relations between these symbols, which can then be analyzed. Another, equivalent, technique to obtain starting phases is the use of magic integers (Main, 1977), which also leads to relations between symbols. Alternatively, phases can be assigned numerical values chosen at random. Subsequent refinement, using (1.24) or (1.29), then usually leads to a convergent set of phases. In the initial stages of this refinement procedure, only structure factors with large $|E|$ values, for example $|E| > 1.3$, are allowed to participate.

Problems with direct methods usually originate from a nonrandom distribution of atoms in the unit cell. For example, the unit cell may contain groups of atoms that slightly differ from one another in composition and/or orientation. These groups can be related to one another by a pseudo translation $\mathbf{t}$. Such a structure is called a superstructure. The pseudo translation causes reflections $\mathbf{H}$ for which $\mathbf{H}\cdot\mathbf{t}$ is not an integer to be nearly extinct. These reflections are thus very weak compared to reflections for which $\mathbf{H}\cdot\mathbf{t}$ is an integer. (They would be extinct if $\mathbf{t}$ was a true symmetry operation.) As a result, the diffraction pattern of the superstructure shows an abundance of reflections that are mostly weak. These reflections require special statistical treatment, otherwise they cannot be phased by direct-methods procedures. This superstructure problem is closely related to a similar problem for aperiodic crystals which also have diffraction patterns that show large numbers of mostly weak reflections (satellites).

1.2 Aperiodic crystals

The X-ray diffraction pattern of a crystal that is periodic in three dimensions shows diffraction spots (Bragg peaks) that can be indexed with three integers: (h_1, h_2, h_3). The spots are said to be situated at the nodes of a three-dimensional reciprocal lattice.

Many crystals (both natural and synthetic ones) show X-ray diffraction patterns that do not conform to this picture, although their diffraction patterns show diffraction spots that are usually well separated from one another. (See Figure 1.1 for an example.) Indexing these spots requires more than three integers: $(h_1, \ldots, h_{3+d})$, where d is the number of extra indices ($d \geq 1$). It is impossible to define a single three-dimensional lattice so that all spots correspond to nodes of that lattice. Obviously, these crystals are not periodic in three-dimensions. However, the appearance of diffraction spots indicates that long-range order does exist in these crystals.

For a diffraction pattern indexed with $(3+d)$ integers, the corresponding crystal can be considered as embedded in $(3+d)$-dimensional superspace, resulting in a supercrystal having $(3+d)$-dimensional lattice periodicity. The crystal in three-dimensional physical space is obtained as the restriction of the supercrystal to a three-dimensional section through superspace. Although this crystal does not have three-dimensional lattice symmetry in physical space, it can be approximated up to arbitrary precision by a three-dimensionally periodic structure. A crystal with this property is called aperiodic. The diffraction pattern of an aperiodic crystal in physical space is obtained as the perpendicular projection of the $(3 + d)$-dimensional reciprocal lattice in superspace onto physical space. This leads to the peculiar diffraction pattern described above. Three types of aperiodic crystals are commonly distinguished.

(i) An incommensurately modulated crystal can be considered as a three-dimensionally periodic crystal (the basic structure), upon which a periodic variation (the modulation) is superimposed. The periodicity of the modulation is incommensurate with respect to the lattice of the basic structure.

(ii) An incommensurate intergrowth compound can be approximated by a coherent combination of two or more three-dimensionally periodic structures (substructures) with, however, mutually incommensurate lattices and hence mutually induced incommensurate modulations. An incommensurate intergrowth compound can be considered as a combination of two or more incommensurately modulated subsystems.

(iii) A quasicrystal is a crystal that can no longer be described in terms of a combination of three-dimensionally periodic structures. Some quasicrystals can be described in three-dimensional physical space as a space-filling assembly of two different unit cells (tilings).

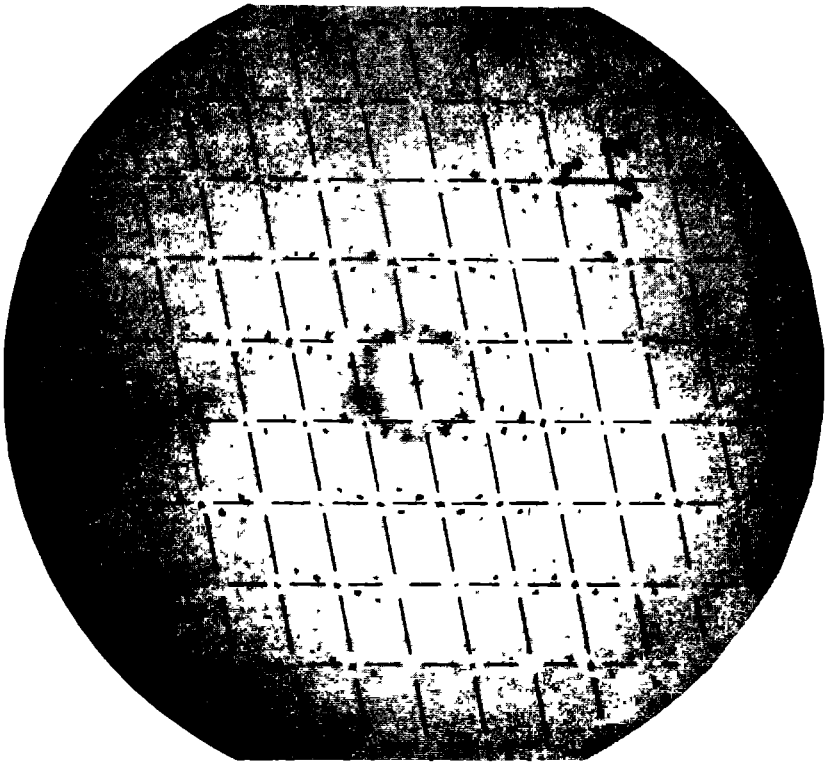


Figure 1.1. Section $h_2 = 3$ of the reciprocal lattice of incommensurate Na_2CO_3. The main reflections are at the nodes of the reciprocal lattice The satellite reflections do not belong to that lattice. The vector $\mathbf{q}^*$, which describes the positions of the satellites, is incommensurate with respect to the reciprocal lattice of the main reflections [Taken from van Aalst, den Hollander, Peterse & de Wolff (1976)]

Quasicrystals are usually recognized by the appearance of noncrystallographic pointgroup symmetry in their diffraction patterns, *e.g.* 5-, 8-, 10- or 12-fold rotation axes.

Diffraction patterns of crystals of type (i) contain strong main reflections, at the nodes of a three-dimensional reciprocal lattice, accompanied by satellite reflections that are usually weaker. (See Figure 1.1 for an example.) For type (ii), the main reflections result from two or more three-dimensional mutually incommensurate reciprocal lattices, partly coinciding. For crystals of type (iii), the distinction between main and satellite reflections no longer exists.

To obtain a better understanding of the nature of aperiodic crystals and their peculiar diffraction patterns, consider the following example of a one-dimensional incommensurate crystal.

In two-dimensional 'superspace', a direct lattice Σ is spanned by the vectors $\{\mathbf{b}_1, \mathbf{b}_2\}$. The corresponding reciprocal lattice Σ^* is spanned by the vectors $\{\mathbf{b}_1^*, \mathbf{b}_2^*\}$, where the $\mathbf{b}_i^*$ are defined through $\mathbf{b}_i \cdot \mathbf{b}_j^* = \delta_{ij}$. The two-dimensional electron density σ is periodic with respect to the lattice Σ, *i.e.* $\sigma(\mathbf{x} + \mathbf{l}) = \sigma(\mathbf{x})$ for all points $\mathbf{x} = x_1\,\mathbf{b}_1 + x_2\,\mathbf{b}_2$ in the plane of the lattice and for all direct-lattice vectors $\mathbf{l} \in \Sigma$. (Note: no assumption is made on the specific form of the 'atoms' in superspace.) Consequently, σ can be written as a Fourier summation

$$\sigma(\mathbf{x}) = \sum_{\mathbf{h}} \hat{\sigma}(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \tag{1.31}$$

where $\mathbf{h} = h_1\,\mathbf{b}_1^* + h_2\,\mathbf{b}_2^*$ (h_1, h_2 integers) is a reciprocal-lattice vector in superspace, $\hat{\sigma}(\mathbf{h})$ is a structure factor and the summation extends over all $\mathbf{h} \in \Sigma^*$. The X-ray diffraction pattern of σ shows reflections at positions that correspond to nodes of the reciprocal lattice Σ^*. Each reflection in superspace can be indexed uniquely with two integer indices (h_1, h_2).

Furthermore, consider the one-dimensional 'physical' space defined by the line $\mathbf{x}_\alpha = x_1\,\mathbf{a}_1$, where $\mathbf{a}_1 = \mathbf{b}_1 + \alpha\,\mathbf{b}_2$. For incommensurate crystals, α is an irrational number. In physical space, a direct lattice Λ is spanned by the vector $\mathbf{a}_1$. The corresponding reciprocal lattice Λ^* is spanned by $\mathbf{a}_1^*$, where $\mathbf{a}_1^* = \mathbf{a}_1/|\mathbf{a}_1|^2$. The one-dimensional electron density ρ, which is the restriction of the two-dimensional electron density σ to physical space, can be obtained from (1.31) as

$$\begin{aligned} \rho(x_1) &\equiv \sigma(\mathbf{x}_\alpha) \\ &= \sum_{\mathbf{h}} \hat{\sigma}(\mathbf{h}) \exp[-2\pi i (h_1 + h_2\alpha) x_1)]. \end{aligned} \tag{1.32}$$

Because the structure is incommensurate (α is irrational), the electron density ρ has no translational symmetry in physical space, *i.e.* $\rho(x_1 + 1) \neq \rho(x_1)$, although ρ can still be

written as a Fourier summation. Because ρ is obtained as a section through σ, the Fourier transform of ρ can be obtained as the perpendicular projection of the Fourier transform of σ onto physical space. Thus, the diffraction vectors $\mathbf{S}$, which describe the diffraction pattern of ρ in physical space, are obtained as perpendicular projections onto physical space of the diffraction vectors $\mathbf{h}$ in superspace: $\mathbf{S} = \mathbf{H} + h_2\,\mathbf{q}$, where $\mathbf{H} = h_1\,\mathbf{a}_1^*$ belongs to the reciprocal lattice Λ^* and $\mathbf{q} = \alpha\,\mathbf{a}_1^*$. For an incommensurate structure, $h_2\,\mathbf{q} \notin \Lambda^*$ which means that the diffraction pattern of ρ in physical space contains many reflections that cannot be associated with nodes of the reciprocal lattice Λ^*. For incommensurate structures, there exists a one-to-one correspondence between diffraction vectors $\mathbf{h}$ in superspace and diffraction vectors $\mathbf{S}$ in physical space. As a result, for a given $\mathbf{q}$, reflections in physical space can be indexed uniquely with the integer indices (h_1, h_2) of the diffraction vector $\mathbf{h}$ in superspace. Here, $\mathbf{q}$ can be regarded as an extra 'independent' reciprocal-lattice vector in physical space, which is necessary to describe the entire diffraction pattern with integer indices. Two types of reflections can be distinguished in the diffraction pattern of ρ in physical space: main reflections ($h_2 = 0$) which can be found at the nodes of the reciprocal lattice Λ^* and satellite reflections ($h_2 \neq 0$) which do not belong to this lattice.

The one-dimensional electron density ρ can be rewritten as (1.32)

$$\rho(x_1) = \sum_{\mathbf{S}} F(\mathbf{S}) \exp(-2\pi i \mathbf{S} \cdot \mathbf{x}_\alpha), \tag{1.33}$$

where $F(\mathbf{S}) = \hat{\sigma}(\mathbf{h})$ is the structure factor and the summation extends over all diffraction vectors $\mathbf{S}$ in physical space.

In summary, an electron density $\rho(x_1)$ in one-dimensional physical space, which can be considered as a section through an electron density $\sigma(\mathbf{x})$ that is periodic in two-dimensional superspace, leads to a diffraction pattern in physical space that consists of main reflections and satellite reflections. These reflections can be indexed uniquely with two integer indices.

Several review papers about aperiodic crystals are available in the literature, a few are given here. The reader is referred to Janssen, Janner, Looijenga-Vos & de Wolff (1992) for incommensurately modulated crystals, to van Smaalen (1992) for incommensurate intergrowth compounds, to Steurer (1990) for quasicrystals and to van Smaalen (1994) for a general review about aperiodic crystals.

1.3 Scope of this thesis

Nowadays, many conventional crystal structures are analyzed by routine application of computerized direct-methods procedures which employ phase relations to solve the phase

problem in X-ray crystallography. However, a straightforward application of these classical methods to aperiodic crystals is impossible because, as discussed above, the X-ray diffraction pattern of such a crystal contains an abundance of (mostly) weak reflections, the satellite reflections. The statistical methods underlying many direct-methods procedures for conventional crystal structures cannot properly handle these extra reflections because the statistical behavior of these reflections was not known.

The goal of the research project, where this thesis is part of, is the development of computerized direct-methods procedures for the routine application of direct methods and Patterson methods to solve the phase problem for aperiodic crystals. Here, only incommensurately modulated structures and misfit layer compounds (a special type of incommensurate intergrowth compounds), that can be regarded as periodic structures in four-dimensional superspace ($d = 1$), have been considered. Direct methods for incommensurately modulated structures were first proposed by Hao, Liu & Fan (1987). They applied a modified version of the Sayre equation to the X-ray diffraction data of incommensurate Na_2CO_3, employing ordinary structure factors (F), instead of normalized structure factors (E), for estimating the importance of the various terms of the Sayre equation. In the present thesis, the extension of the *statistical* methods underlying the various direct-methods procedures to aperiodic crystals has been initiated. In particular, the statistical background is developed for the definition of normalized structure factors for crystals with an incommensurate one-dimensional modulation (Chapters 2-4). The usefulness of these normalized structure factors in relation to direct methods is investigated by tests on several incommensurately modulated structures (Chapters 5 and 6). In addition, in Chapters 7 and 8 of this thesis, a multidimensional Sayre equation is derived for incommensurate intergrowth compounds. Finally, in Chapter 9 of this thesis, it is shown that misfit layer compounds can also be solved by automated Patterson techniques. Considering the scope of the entire research project, this thesis can be regarded as a first but important step towards the application of statistical methods to aperiodic crystals.

References

AALST, W. VAN, HOLLANDER, J. DEN, PETERSE, W. J. A. M. & WOLFF, P. M. DE (1976). *Acta Cryst.* B**32**, 47–58.

BEURSKENS, P. T. (1963). *Technical Report on Sign Correlation by the Sayre Equation.* The Crystallography Laboratory, University of Pittsburgh, Pennsylvania.

BEURSKENS, P. T. (1964). *Acta Cryst.* **17**, 462.

COCHRAN, W. (1955). *Acta Cryst.* **8**, 473–478.

COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1–12.

GIACOVAZZO, C. (1980). *Direct Methods in Crystallography.* London: Academic.

GIACOVAZZO, C., MONACO, H. L., VITERBO, D., SCORDARI, F., GILLI, G., ZANOTTI, G. & CATTI, M. (1992). *Fundamentals of Crystallography. IUCr Texts on Crystallography* 2. Edited by C. Giacovazzo. Oxford: University Press.

HAO, Q., LIU, Y.-W. & FAN, H.-F. (1987). *Acta Cryst.* A**43**, 820–824.

JANSSEN, T., JANNER, A., LOOIJENGA-VOS, A. & WOLFF, P. M. DE (1992). *International Tables for Crystallography.* Volume C, edited by A. J. C. Wilson. Dordrecht: Kluwer Academic.

KARLE, J. & KARLE, I. (1966). *Acta Cryst.* **21**, 849–859.

MAIN, P. (1977). *Acta Cryst.* A**33**, 750–757.

RAMACHANDRAN, G. N. & SRINIVASAN, R. (1959). *Acta Cryst.* **12**, 410–411.

SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.

SMAALEN, S. VAN (1992). *Mater. Sci. Forum*, **100&101**, 173–222.

SMAALEN, S. VAN (1994). *Crystallography Reviews.* In press.

STEURER, W (1990). *Z. Kristallogr.* **190**, 179–234.

WILSON, A. J. C. (1942). *Nature (London)* **150**, 151–152.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

2

Scaling of X-Ray Diffraction Intensities for Crystals with a One-Dimensional Incommensurate Displacive Modulation*

Abstract

A statistical method is presented for the determination of a scale factor, an overall isotropic temperature factor and an overall modulation amplitude from the X-ray diffraction intensities of crystals with a one-dimensional incommensurate displacive modulation. Application to several compounds with a known modulation illustrates the accuracy of our method. The results may provide a starting point for a structure determination. A preliminary definition is given of normalized structure factors, which can be used in direct methods for the solution of the phase problem.

*Published as: Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1992). *Solid State Communications*, **82**, 345–349.

2.1 Introduction

An incommensurately modulated crystal consists of a basic structure which has three-dimensional translational symmetry and a periodic deviation superimposed upon this basic structure. The wavelength of the deviation is not compatible with the lattice of the basic structure. The diffraction pattern of such a crystal consists of strong main reflections accompanied by weaker satellite reflections. The intensity of a main reflection is mainly determined by the presence of atoms at their average positions in the basic structure, while the intensity of a satellite reflection essentially depends on the degree of distortion from the basic structure.

For conventional crystals there exists a statistical method developed by Wilson [1] to obtain a scale factor and an overall isotropic temperature factor from X-ray diffraction data. The results are then used to bring the intensities from a relative to an absolute scale and to calculate normalized structure factors. Because of the different behavior of the intensities of main and satellite reflections, this method cannot be used for modulated structures.

In this paper, we propose a method for incommensurate one-dimensionally displacively modulated structures which resembles Wilson's method and which allows the determination not only of a scale factor and an overall isotropic temperature factor, but also of an overall value for the modulation amplitude.

2.2 Theory

Let the unit cell of the basic structure be spanned by vectors $\mathbf{a}_i$ $(i = 1, 2, 3)$. The reciprocal basic vectors $\mathbf{a}_i^*$ $(i = 1, 2, 3)$ are defined by $\mathbf{a}_i^* \cdot \mathbf{a}_j = \delta_{ij}$. For an incommensurate one-dimensionally displacively modulated crystal, the position of a reflection in reciprocal space is given by the diffraction vector $\mathbf{S} = \sum_{i=1}^{3} S_i \, \mathbf{a}_i^*$ with components $S_i = H_i + mq_i$, where q_i is a coordinate of the modulation wave vector $\mathbf{q} = \sum_{i=1}^{3} q_i \, \mathbf{a}_i^*$. This vector is incommensurate with respect to the reciprocal lattice of the basic structure. The H_i's and m are integers with $|m|$ being the satellite order. The length of $\mathbf{S}$ is given by $S = 2(\sin\theta)/\lambda = 2s$. There are two types of reflections: main reflections $(m = 0)$ and satellite reflections $(m \neq 0)$.

An expression for the structure factor is [2,3]

$$F(\mathbf{S}) = \sum_{\mu=1}^{N} g_\mu(\mathbf{S}) f_\mu(\mathbf{S}) \exp[2\pi i(\mathbf{S} - m\mathbf{q}) \cdot \mathbf{r}_0^\mu], \tag{2.1}$$

where the summation extends over all atoms (N) in the unit cell of the basic structure. The

μth atom is found at average position $\mathbf{r}_0^\mu$. The effect of the modulation on the diffraction intensity is given by the atomic modulation factor $g_\mu(\mathbf{S})$:

$$g_\mu(\mathbf{S}) = \int_0^1 \exp[2\pi i\{\mathbf{S}\cdot\mathbf{u}_\mu(\tau) + m\tau\}]\,\mathrm{d}\tau, \tag{2.2}$$

where $\mathbf{u}_\mu[\mathbf{q}\cdot(\mathbf{r}_0^\mu + \mathbf{L})]$ is a periodic function with period 1, which gives the displacement of the μth atom in unit cell $\mathbf{L}$. In first approximation, $\mathbf{u}_\mu$ can be taken as a harmonic function,

$$\mathbf{u}_\mu[\mathbf{q}\cdot(\mathbf{r}_0^\mu + \mathbf{L})] = \sum_{i=1}^{3} U_i^\mu \sin[2\pi\mathbf{q}\cdot(\mathbf{r}_0^\mu + \mathbf{L}) - \alpha_i^\mu]\,\mathbf{a}_i, \tag{2.3}$$

where U_i^μ and α_i^μ are three amplitudes and three phases describing the modulation of atom μ. The harmonic approximation means that the analysis is essentially restricted to main reflections and first-order satellites. The atomic form factor $f_\mu(\mathbf{S})$ may be approximated by

$$f_\mu(\mathbf{S}) = f_{0\mu}(s)\exp(-Bs^2), \tag{2.4}$$

where $f_{0\mu}(s)$ is the atomic form factor for atoms at rest and B is an overall isotropic temperature parameter.

Substitution of (2.3) in (2.2) gives

$$g_\mu(\mathbf{S}) = J_m[2\pi C_\mu(\mathbf{S})]\exp(im[\eta_\mu(\mathbf{S}) + \pi]), \tag{2.5}$$

where J_m is the mth order Bessel function and $C_\mu(\mathbf{S})$ and $\eta_\mu(\mathbf{S})$ are defined by the transformation [4]

$$\mathbf{S}\cdot\mathbf{U}_c^\mu = C_\mu(\mathbf{S})\cos[\eta_\mu(\mathbf{S})], \quad \mathbf{S}\cdot\mathbf{U}_s^\mu = C_\mu(\mathbf{S})\sin[\eta_\mu(\mathbf{S})] \tag{2.6}$$

with $C_\mu(\mathbf{S}) \geq 0$ and with the vectors $\mathbf{U}_c^\mu$ and $\mathbf{U}_s^\mu$ given by

$$\mathbf{U}_c^\mu = \sum_{i=1}^{3} U_i^\mu \cos(\alpha_i^\mu)\,\mathbf{a}_i, \quad \mathbf{U}_s^\mu = \sum_{i=1}^{3} U_i^\mu \sin(\alpha_i^\mu)\,\mathbf{a}_i. \tag{2.7}$$

From transformation (2.6), the following expression can be derived:

$$C_\mu(\mathbf{S}) = 2s\left([U_c^\mu\cos\{\delta_c^\mu(\mathbf{S})\}]^2 + [U_s^\mu\cos\{\delta_s^\mu(\mathbf{S})\}]^2\right)^{1/2}, \tag{2.8}$$

where $\delta_c^\mu(\mathbf{S})$ is the angle between $\mathbf{S}$ and $\mathbf{U}_c^\mu$ and, similarly, $\delta_s^\mu(\mathbf{S})$ is the angle between $\mathbf{S}$ and $\mathbf{U}_s^\mu$. The length of a vector $\mathbf{U}$ is denoted U. From (2.6) and (2.7), it can be shown that (2.8) is equivalent to

$$C_\mu(\mathbf{S}) = \left(\sum_{i,j=1}^{3} S_i U_{ij}^\mu S_j\right)^{1/2}, \tag{2.9}$$

where

$$U_{ij}^{\mu} = U_i^{\mu} U_j^{\mu} \cos(\alpha_i^{\mu} - \alpha_j^{\mu}) \tag{2.10}$$

is the ijth component of a symmetric modulation tensor for the μth atom.

Substitution of (2.4) and (2.5) in (2.1) leads to an expression for the intensities $|F(\mathbf{S})|^2$ as a function of $\mathbf{S}$, B, U_i^{μ}, α_i^{μ} and $\mathbf{r}_0^{\mu}$. In a procedure analogous to Wilson [1], the average of $|F(\mathbf{S})|^2$ can be calculated over all reflections at constant s. However, for each reflection order $|m|$, the average is computed separately.

Assume that sufficient reflections are present in the s interval so that the cross terms in $|F(\mathbf{S})|^2$ cancel. Furthermore, the dependence of $f_{0\mu}(s)$ on s is assumed to be equal for all atoms. Then, the averaged intensities can be written as

$$\begin{aligned} \left\langle |F(\mathbf{S})|^2 \right\rangle_{s,|m|} &= \left[\sum_{\mu=1}^{N} f_{0\mu}^2(s) \right] \exp(-2Bs^2) \times \\ &\quad \left\langle \frac{1}{\sigma} \sum_{\mu=1}^{N} Z_{\mu}^2 J_{|m|}^2[2\pi C_{\mu}(\mathbf{S})] \right\rangle_{s,|m|}, \end{aligned} \tag{2.11}$$

where Z_{μ} is the atomic number of atom μ and $\sigma = \sum_{\mu=1}^{N} Z_{\mu}^2$.

The summation in the last factor of (2.11) can be considered as a squared-atomic-number weighted average of the Bessel functions over all atoms in the unit cell. It can be approximated as follows.

First, replace the factor $\langle \cdots \rangle_{s,|m|}$ in (2.11) by $(4\pi)^{-1} \int_{\Omega} \cdots \, \mathrm{d}\Omega$, where the integral extends over all orientations of $\mathbf{S}$ at constant s, *i.e.* change the discrete distribution into a continuous one. Then, consider the case of all atoms having the same modulation parameters, *i.e.* $U_i^{\mu} = U_i$ and $\alpha_i^{\mu} = \alpha_i$, so that $C_{\mu}(\mathbf{S}) = C(\mathbf{S})$. If, in addition, $\alpha_i = \alpha_1 + n_i \pi$ with n_i an integer, this modulation is also linear, *i.e.* for all atoms μ, the displacement vectors $\mathbf{u}_{\mu}[\mathbf{q} \cdot (\mathbf{r}_0^{\mu} + \mathbf{L})]$ as a function of $\mathbf{L}$ are always parallel to a fixed direction. Therefore, we can write $C(\mathbf{S}) = 2sU\cos(\delta)$, where δ is the angle between $\mathbf{S}$ and $\mathbf{U} = \sum_{i=1}^{3} (-1)^{n_i} U_i \, \mathbf{a}_i$. The factor at hand is then equal to

$$Z(s; |m|, U) = \int_0^1 J_{|m|}^2(4\pi s U x) \, \mathrm{d}x. \tag{2.12}$$

The averaged intensity can now be written as

$$\left\langle |F(\mathbf{S})|^2 \right\rangle_{s,|m|} = \left[\sum_{\mu=1}^{N} f_{0\mu}^2(s) \right] \exp(-2Bs^2) \, Z(s; |m|, U). \tag{2.13}$$

The function $Z(s; |m|, U)$ can be evaluated numerically. A few graphs are shown in Figure 2.1.

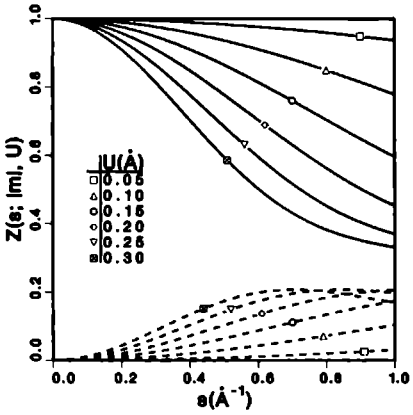


Figure 2.1. The function $Z(s;|m|,U)$ [see equation (2.12)] as function of s plotted for reflection orders $m = 0$ (solid curves) and $|m| = 1$ (dashed curves) and several values of the overall modulation amplitude U.

It can be shown, by series expansion of $J_{|m|}$, that (2.11) (written as a continuous distribution) for a general displacement field and (2.13) for the special 'equal-modulation' case are identical up to second order in all amplitudes U_i^μ and U provided

$$U^2 = \frac{1}{\sigma}\sum_{\mu=1}^{N} Z_\mu^2[(U_c^\mu)^2 + (U_s^\mu)^2]. \tag{2.14}$$

It is clear therefore, that for a not too large modulation, equation (2.13) holds for the general case. We call U, as given by (2.14), the overall modulation amplitude.

So far, we did not consider any symmetry but, there is one symmetry effect which must be taken into account. That is the symmetry enhancement factor $\epsilon(\mathbf{S})$ which can be defined as for conventional crystals [5].

We define the partially normalized structure factor by

$$E_a(\mathbf{S}) = F(\mathbf{S})\left[\epsilon(\mathbf{S})\sum_{\mu=1}^{N} f_{0\mu}^2(s)\right]^{-1/2} \tag{2.15}$$

and we can write its mean square [see equation (2.13)] as

$$\left\langle |E_a(\mathbf{S})|^2 \right\rangle_{s,|m|} = \exp(-2Bs^2)\, Z(s;|m|,U). \tag{2.16}$$

Because the intensities $I(\mathbf{S})$ obtained from an experiment, corrected for Lorentz and polarization effects and absorption, are on a relative scale, we define the scale factor K by

$$|F(\mathbf{S})|^2 = K^2 I(\mathbf{S}). \tag{2.17}$$

Thus, for the observed average of $|E_a(\mathbf{S})|^2$ on a relative scale, denoted $G(s;|m|)$, we have

$$\begin{aligned} G(s;|m|) &\equiv \left\langle I(\mathbf{S}) \left[\epsilon(\mathbf{S}) \sum_{\mu=1}^{N} f_{0\mu}^2(s) \right]^{-1} \right\rangle_{s,|m|} \\ &= K^{-2} \exp(-2Bs^2)\, Z(s;|m|,U). \end{aligned} \tag{2.18}$$

After sorting the reflections into suitable s intervals for given $|m|$, equation (2.18) is used in a fitting procedure to determine the scale factor K, the overall isotropic temperature factor B and the average modulation amplitude U.

2.3 Numerical results

Fitting according to (2.18) was done with the Marquardt [6] non-linear least-squares procedure. Starting values for K and B were obtained from a Wilson plot [1] using main reflections only, the starting value for U was chosen to be 0.001 Å. The fitting procedure has been tested for several compounds for which the modulation is known. Tests were performed using structure factors calculated from the published structural parameters (up to $s = 1$ Å^{-1}), as well as observed X-ray intensities.

Suitable s intervals were created by dividing the reciprocal space into shells of equal volume; all reflections were sorted into these intervals. In a progressive averaging procedure, each interval was combined with its two neighboring intervals. In this way, we obtained a distribution $G(s;|m|)$ for each order $|m|$.

In principle, one must use all reflections up to a certain cutoff value in s. However, a number of 'unobserved' reflections, omitted from the experimental data set, were taken into account by giving them an intensity equal to one quarter of the mean intensity of the 10 weakest symmetry-independent reflections in that particular interval.

For each compound, the overall modulation amplitude U was obtained from the published modulation amplitudes by use of (2.14). Similarly, the overall temperature parameter B was calculated from the published structure parameters as an average over equivalent temperature parameters [7] weighted with squared atomic numbers. The scale factor for the structure factors calculated from the published structural parameters is 1 by definition.

For several compounds with small and large modulations the results are summarized in Table 2.1. Apparently all scale factors are overestimated. As expected, because of the large correlation between displacive modulation and thermal motion, the B values from the Wilson plot are higher than the B values from our fitting procedure (except for

Table 2.1. Parameters K, B and U obtained from the published structure and with the fitting procedure. Columns I: using calculated reflection intensity data based on published structural parameters. Columns II: using experimental data. For each compound, line (t) contains B and U calculated from published parameters; for calculated data, $K = 1$. For experimental data, K is unknown. Line (W) contains the results obtained from a Wilson plot applied to main reflections only and line (f) shows the results obtained from a fitting procedure employing (2.18) applied to main and first-order reflections.

		I: calculated data			II: experimental data			
compound		K	B(Å^2)	U(Å)	K	B(Å^2)	U(Å)	references
	t	1	0.22	0.033		0.22	0.033	
$K_{0.3}MoO_3$	W	1.06	0.14		3.27	0.14		[8]
	f	1.06	0.13	0.034	3.29	0.12	0.034	
	t	1	0.40	0.046		0.40	0.046	
Mo_8O_{23}	W	1.02	0.34		0.442	0.31		[9]
	f	1.03	0.33	0.027	0.443	0.30	0.025	
	t	1	0.55	0.096		0.55	0.096	
K_2SeO_4	W	1.06	0.47		1.11	0.34		[10,11]
	f	1.05	0.40	0.076	1.12	0.25	0.078	
	t	1	0.99	0.112				
$C_{12}D_{10}$†	W	1.03	0.95					[12]
	f	1.02	0.75	0.110				
	t	1	0.69	0.169‡		0.69	0.169‡	
$NbTe_4$	W	1.06	0.93		1.95	0.84		[13,14]
	f	1.05	0.63	0.163	2.03	0.44	0.172	
	t	1	4.72	0.287				
Rb_2ZnBr_4	W	1.46	2.87					[15]
	f	1.18	3.17	0.175				
	t	1	1.42	0.386		1.42	0.386	
Na_2CO_3	W	1.44	1.54		0.83	1.61		[16]
	f	1.07	1.14	0.388	0.64	1.06	0.424	
	t	1	6.29	1.154		6.29	1.154	
PTZ-TCNQ§	W	1.69	4.73		2.55	4.09		[17]
	f	1.18	3.54	0.785	2.04	3.38	0.442	

†Deuterated biphenyl.

‡If second-order harmonics are taken into account, $U = 0.178$Å.

§$(C_{12}H_9NS)\cdot(C_{12}H_4N_4)$.

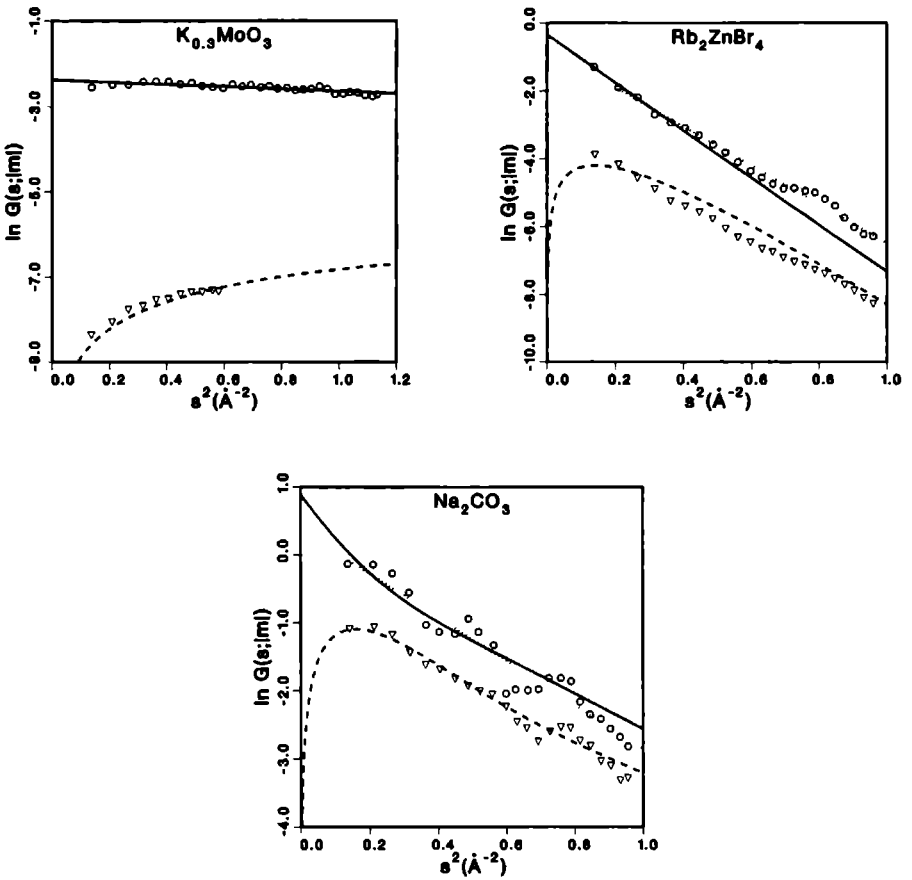


Figure 2.2. Intensity distributions and fitted functions (see equation 2.18) for three test cases. The data points are given by circles for $m = 0$ and triangles for $|m| = 1$, the fitted functions are given by solid lines and dashed lines respectively. The dotted line results from a Wilson plot applied to main reflections only.

Rb_2ZnBr_4). For compounds with large modulations, our fitting procedure gives a very much improved scale factor. Most results obtained for B and U are in good agreement with the *a priori* calculated values [given at lines (t)]; also for the case of $NbTe_4$, where second-order harmonics are not without importance. It can be shown theoretically that the correction to the mean intensities due to small higher-order harmonics can be simulated by the temperature factor. The U values in columns (I) and (II) are essentially equal, which justifies our treatment of missing ('unobserved') reflections. Thus, as can be seen from Table 2.1, for each compound, the U value obtained from our fitting procedure is in close agreement with the value calculated from the known structural parameters, except for PTZ–TCNQ.

From Figure 2.2, one can see that the intensity distributions are reasonably well reproduced by (2.18). The plots for $K_{0.3}MoO_3$ and Na_2CO_3 are typical for all test cases; Rb_2ZnBr_4 is much worse, but PTZ–TCNQ (not shown) is an extreme exception.

PTZ–TCNQ does have a very large modulation amplitude and the calculated intensity distribution of the main reflections shows a minimum at $s = 0.7$ Å^{-1}, while $Z(s;0,U)$ (Figure 2.1) decreases monotonously. Therefore, in Table 2.1 (columns I) data up to $s = 0.64$ Å^{-1} are used. As our theoretical results are derived for small modulations, the results for PTZ–TCNQ have qualitative meaning only. (Note that the experimental data set contains only about 18% observed reflections.) In general, our fitting procedure works well when modulations are a few tenth of an angstrom.

2.4 Concluding remarks

A method is proposed for scaling X-ray diffraction intensities of incommensurate one-dimensionally displacively modulated crystals. The method generally results in a reliable approximation of the measured intensity distribution. The modulation is characterized by a single overall modulation amplitude (2.14). The latter may provide a starting point for the refinement of these structures.

Conventional direct-methods procedures critically depend on the use of normalized structure factors [18]. First applications of direct methods to incommensurate structures employed $|F(\mathbf{S})|$ instead of normalized structure factors [19,20], as a definition of the latter was not yet available.

Our fitting procedure (2.18) allows for a preliminary definition of normalized structure factors for crystals with an incommensurate one-dimensional displacive modulation:

$$E_b(\mathbf{S}) \;=\; F(\mathbf{S})\exp(Bs^2)\times$$

$$\left[\epsilon(\mathbf{S})\, Z(s;|m|,U) \sum_{\mu=1}^{N} f_{0\mu}^2(s)\right]^{-1/2} \tag{2.19}$$

They can be used for the computerization of various direct-methods procedures for modulated crystals for the case where the modulation does not give anisotropic effects in reciprocal space. In the general case, where orientational dependency is of importance, equation (2.9) may be the basis for a final definition of $E(\mathbf{S})$ values.

Acknowledgements

We thank A. Janner (University of Nijmegen) for many stimulating discussions, F. Tuinstra (Delft University of Technology) for supplying the experimental data of Na_2CO_3 and Noburu Yamada (Tohoku University) for supplying the experimental data of K_2SeO_4. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO). Financial support by the Royal Netherlands Academy of Arts and Sciences (KNAW) is acknowledged.

References

[1] A. J. C. Wilson, *Nature (London)* **150**, 151 (1942).

[2] P. M. De Wolff, *Acta Cryst.* **A30**, 777 (1974).

[3] A. Yamamoto, *Acta Cryst.* **A38**, 87 (1982).

[4] V. Petříček & P. Coppens, *Acta Cryst.* **A44**, 235 (1988).

[5] A. J. C. Wilson, *Acta Cryst.* **3**, 258 (1950).

[6] J. Kowalik & M. R. Osborne, *Methods for Unconstrained Optimization Problems*, Elsevier, New York (1968).

[7] W. C. Hamilton, *Acta Cryst.* **12**, 609 (1959).

[8] W. J. Schutte, *Structures of Modulated Crystals*, thesis, University of Groningen, Groningen (1990).

[9] A. J. H. Komdeur, J. L. de Boer & S. van Smaalen, *J. Phys.: Condens. Matter* **2**, 45 (1990).

[10] N. Yamada & T. Ikeda, *J. Phys. Soc. Jap.* **53**, 2555 (1984).

[11] N. Yamada, *Private communication* (1991): The cell dimensions of K_2SeO_4 at 113 K are $a = 7.561$ Å, $b = 10.314$ Å, $c = 5.952$ Å and $\mathbf{q} = 0.32\mathbf{a}^*$.

[12] J. L. Baudour & M. Sanquer, *Acta Cryst.* **B39**, 75 (1983).
[13] S. van Smaalen, K. D. Bronsema & J. Mahy, *Acta Cryst.* **B42**, 43 (1986).
[14] The modulation parameter B_1 for Nb should be $-.03899(22)$.
[15] A. C. R. Hogervorst & R. B. Helmholdt, *Acta Cryst.* **B44**, 120 (1988).
[16] W. van Aalst, J. den Hollander, W. J. A. M. Peterse & P. M. de Wolff, *Acta Cryst.* **B32**, 47 (1976).
[17] H. Kobayashi, *Acta Cryst.* **B30**, 1010 (1974).
[18] J. Karle & I. L. Karle, *Acta Cryst.* **21**, 849 (1966).
[19] Q. Hao, Y.-W. Liu & H.-F. Fan, *Acta Cryst.* **A43**, 820 (1987).
[20] S.-B. Xiang, H.-F. Fan, X.-J. Wu & F.-H. Li, *Acta Cryst.* **A46**, 929 (1990).

3

A More General Expression for the Average X-Ray Diffraction Intensity of Crystals with an Incommensurate One-Dimensional Modulation*

Abstract

Statistical methods are used to derive an expression for the average X-ray diffraction intensity, as function of $(\sin\theta)/\lambda$, of crystals with an incommensurate one-dimensional modulation. Displacive and density modulations are considered, as well as a combination of these two. The atomic modulation functions are given by truncated Fourier series that may contain higher-order harmonics. The resulting expression for the average X-ray diffraction intensity is valid for main reflections and low-order satellite reflections. The modulation of individual atoms is taken into account by the introduction of overall modulation amplitudes. The accuracy of this expression for the average X-ray diffraction intensity is illustrated by comparison with model structures. A definition is presented for normalized structure factors of crystals with an incommensurate one-dimensional modulation that can be used in direct-methods procedures for solving the phase problem in X-ray crystallography. A numerical fitting procedure is described which can extract a scale factor, an overall temperature parameter and overall modulation amplitudes from experimental reflection intensities.

*Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1994). *Acta Crystallographyca*, **A50**. In press.

3.1 Introduction

For nonmodulated crystals, a statistical method exists which allows for the determination of a scale factor and an overall isotropic temperature parameter from X-ray diffraction data (Wilson, 1942). The results are then used to bring the intensities from a relative to an absolute scale and to calculate normalized structure-factor amplitudes. This method cannot be applied to X-ray diffraction data of incommensurately modulated crystals because of the different behavior of the intensities of main and satellite reflections.

Recently, an expression has been derived for the average X-ray diffraction intensity, as function of $(\sin\theta)/\lambda$, of crystals with an incommensurate one-dimensional displacive modulation (Lam, Beurskens & van Smaalen, 1992*a*). Averages for main reflections and averages for first-order satellites were used together in a fitting procedure similar to Wilson (1942). In this way, a scale factor, an overall isotropic temperature factor and an overall modulation amplitude could be determined directly from the measured intensities. The overall modulation amplitude was interpreted as a weighted average of the individual modulation amplitudes. The results were used to calculate normalized structure-factor amplitudes (Lam, Beurskens, & van Smaalen, 1993). However, because the Fourier series for the displacive modulation were truncated at the first-order harmonic, this expression for the average X-ray diffraction intensity is only valid for main reflections and first-order satellites.

In the present paper, a more general expression is derived for the average X-ray diffraction intensity of incommensurate one-dimensionally modulated crystals. This expression incorporates displacive and density (occupational) modulations and it allows higher-order harmonics in the Fourier series of the modulation functions. The average intensities of satellites of any order can thus be described. The modulation is taken into account by the introduction of one overall modulation amplitude for each harmonic of the displacive modulation and for each harmonic of the density modulation. In addition, the expression for the average X-ray diffraction intensity is used to define normalized structure factors for crystals with an incommensurate one-dimensional modulation.

3.2 Structure-factor formalism

An incommensurately modulated crystal can be considered as a three-dimensional translationally symmetric crystal (the basic structure), upon which a periodic deviation (the modulation) is superimposed. The wavelength of the modulation is incommensurate with

respect to the lattice of the basic structure. Therefore, an incommensurately modulated crystal does not have three-dimensional translational symmetry. However, long range order does exist. The unit cell of the basic structure is spanned by the vectors $\mathbf{a}_i$ $(i = 1, 2, 3)$. The reciprocal basic vectors $\mathbf{a}_i^*$ are defined by $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$. The periodicity of the incommensurate one-dimensional modulation is given by the wave vector $\mathbf{q} = \sum_{i=1}^{3} q_i \mathbf{a}_i^*$, where at least one of the q_i is an irrational number.

Two types of modulations are generally distinguished: displacive modulation and density modulation. If displacive modulation occurs, the positions of the atoms are subject to periodic variations. Let the position of an atom μ in the basic structure be given by $\mathbf{r}_{0,\mathbf{L}}^{\mu} = \mathbf{r}_0^{\mu} + \mathbf{L}$, where $\mathbf{r}_0^{\mu}$ is the position of the atom in the basic-structure unit cell and $\mathbf{L}$ is a basic-structure lattice vector. The position of the same atom in the modulated crystal is then given by $\mathbf{r}_{\mathbf{L}}^{\mu} = \mathbf{r}_{0,\mathbf{L}}^{\mu} + \mathbf{u}^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu})$, where $\mathbf{u}^{\mu}$ describes the atomic displacement. The function $\mathbf{u}^{\mu}$ is periodic and can be written as a truncated Fourier series,

$$\mathbf{u}^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu}) = \sum_{k_u=1}^{K_u} \left[\sum_{i=1}^{3} U_{k_u,i}^{\mu} \sin(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu} - \alpha_{k_u,i}^{\mu}) \mathbf{a}_i \right], \tag{3.1}$$

where $U_{k_u,i}^{\mu}$ and $\alpha_{k_u,i}^{\mu}$ are the three amplitudes and three phases, respectively, of the k_uth harmonic and K_u is the maximum number of harmonics contributing to this series. Equation (3.1) can also be written as

$$\mathbf{u}^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu}) = \sum_{k_u=1}^{K_u} \left[\mathbf{U}_{k_u}^{\mu,c} \sin(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu}) - \mathbf{U}_{k_u}^{\mu,s} \cos(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu}) \right], \tag{3.2}$$

with the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$ given by

$$\mathbf{U}_{k_u}^{\mu,c} = \sum_{i=1}^{3} U_{k_u,i}^{\mu} \cos(\alpha_{k_u,i}^{\mu}) \mathbf{a}_i \tag{3.3}$$

and

$$\mathbf{U}_{k_u}^{\mu,s} = \sum_{i=1}^{3} U_{k_u,i}^{\mu} \sin(\alpha_{k_u,i}^{\mu}) \mathbf{a}_i, \tag{3.4}$$

respectively.

In case of a density modulation, it is the occupancy factor that shows a periodic variation. For an atom at basic-structure position $\mathbf{r}_{0,\mathbf{L}}^{\mu}$, the occupancy factor, $p_{\mathbf{L}}^{\mu} = p^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu})$, can be written as the truncated Fourier series,

$$p^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu}) = P_0^{\mu} + \sum_{k_p=1}^{K_p} P_{k_p}^{\mu} \sin(2\pi k_p \mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu} - \beta_{k_p}^{\mu}), \tag{3.5}$$

where $P^{\mu}_{k_p}$ and $\beta^{\mu}_{k_p}$ are the amplitude and phase, respectively, of the k_pth harmonic, and P^{μ}_0 is the average occupancy factor of atom μ. The maximum number of harmonics contributing to this series is denoted by K_p. Equation (3.5) can be rewritten as

$$p^{\mu}(\mathbf{q}\cdot\mathbf{r}^{\mu}_{0,\mathbf{L}}) = \sum_{k_p=-K_p}^{K_p} p^{\mu}_{k_p}\exp(2\pi i k_p \mathbf{q}\cdot\mathbf{r}^{\mu}_{0,\mathbf{L}}), \tag{3.6}$$

with the complex amplitudes $p^{\mu}_{k_p}$ given by

$$p^{\mu}_{k_p} = \begin{cases} -(iP^{\mu}_{k_p}/2)\exp(-i\beta^{\mu}_{k_p}) & (k_p > 0) \\ P^{\mu}_0 & (k_p = 0) \\ (iP^{\mu}_{-k_p}/2)\exp(i\beta^{\mu}_{-k_p}) & (k_p < 0). \end{cases} \tag{3.7}$$

The diffraction pattern of an incommensurate one-dimensionally modulated crystal consists of main reflections at the nodes of the reciprocal lattice of the basic structure, accompanied by satellite reflections that are usually weaker. Diffraction vectors $\mathbf{S} = \sum_{i=1}^{3} S_i\,\mathbf{a}_i^*$ are defined as $\mathbf{S} = \mathbf{H} + m\mathbf{q}$, where $\mathbf{H} = \sum_{i=1}^{3} H_i\,\mathbf{a}_i^*$ is a diffraction vector of the basic structure and m is the satellite index. This means that, for a given modulation wave vector $\mathbf{q}$, each diffraction vector $\mathbf{S}$ is uniquely characterized by a set of four integers (H_1, H_2, H_3, m).† There are two kinds of reflections: main reflections ($m = 0$) and satellite reflections ($m \neq 0$). The order of a reflection is denoted by $|m|$.

The structure factor for X-ray scattering from a crystal with an incommensurate one-dimensional modulation is written as (de Wolff, 1974; Yamamoto, 1982)

$$F(\mathbf{S},m) = \sum_{\mu=1}^{N} g^{\mu}(\mathbf{S},m) f^{\mu}(\mathbf{S}) \exp[2\pi\imath\,(\mathbf{S} - m\mathbf{q})\cdot\mathbf{r}^{\mu}_0], \tag{3.8}$$

where the summation extends over all atoms (N) in the basic-structure unit cell. The effect of the modulation on the X-ray diffraction intensity is given by the atomic modulation factor

$$g^{\mu}(\mathbf{S},m) = \int_0^1 p^{\mu}(\tau)\exp\{2\pi\imath\,[\mathbf{S}\cdot\mathbf{u}^{\mu}(\tau) + m\tau]\}\,\mathrm{d}\tau, \tag{3.9}$$

where p^{μ} and $\mathbf{u}^{\mu}$ are the atomic modulation functions for the density modulation and the displacive modulation, respectively. The atomic scattering factor f^{μ} may be approximated by

$$f^{\mu}(\mathbf{S}) = f^{\mu}_0(s)\exp(-Bs^2), \tag{3.10}$$

†(H_1, H_2, H_3) are usually denoted (h, k, l).

where f_0^μ is the form factor for atoms at rest, B is an overall isotropic temperature parameter and $s = (\sin\theta)/\lambda = S/2$, with S being the length of the diffraction vector $\mathbf{S}$. For theoretical evaluations, f_0^μ may be approximated by

$$f_0^\mu(s) \simeq Z_\mu \left\{ \frac{1}{\sigma} \sum_{\nu=1}^{N} [f_0^\nu(s)]^2 \right\}^{1/2}, \tag{3.11}$$

where Z_μ is the atomic number and $\sigma = \sum_{\mu=1}^{N} Z_\mu^2$. Note that, assuming no anomalous scattering, the atomic form factor is a real function. From this and from the fact that $g^\mu(\mathbf{S}, m) = [g^\mu(-\mathbf{S}, -m)]^*$, where * denotes the complex conjugate, it follows that Friedel's law applies to the structure factor.

Note that for crystals with density modulation, the atomic form factor f_0^μ may actually represent the scattering factor of an averaged atom. However, this requires proper adjustment of the values of the amplitudes $P^\mu_{|k_p|}$.

3.3 An expression for the average intensity

To derive the expression for the average X-ray diffraction intensity, the atomic modulation factor g^μ is evaluated first. From expression (3.2) for the atomic displacement $\mathbf{u}^\mu$, a straightforward calculation leads to

$$\mathbf{S} \cdot \mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}^\mu_{0,\mathbf{L}}) = \sum_{k_u=1}^{K_u} C^\mu_{k_u}(\mathbf{S}) \sin[2\pi k_u \mathbf{q} \cdot \mathbf{r}^\mu_{0,\mathbf{L}} - \eta^\mu_{k_u}(\mathbf{S})], \tag{3.12}$$

with the amplitude $C^\mu_{k_u}$ and phase $\eta^\mu_{k_u}$ defined by the transformation (Petříček, Coppens & Becker, 1985; Petříček & Coppens, 1988)

$$\begin{cases} \mathbf{S} \cdot \mathbf{U}^{\mu,c}_{k_u} = C^\mu_{k_u}(\mathbf{S}) \cos[\eta^\mu_{k_u}(\mathbf{S})] \\ \mathbf{S} \cdot \mathbf{U}^{\mu,s}_{k_u} = C^\mu_{k_u}(\mathbf{S}) \sin[\eta^\mu_{k_u}(\mathbf{S})] \end{cases} \tag{3.13}$$

and with $C^\mu_{k_u}(\mathbf{S}) \geq 0$. Note that, from (3.13), it follows that $\tan[\eta^\mu_{k_u}(\mathbf{S})]$, and therefore $\eta^\mu_{k_u}(\mathbf{S})$ itself, only depends on the orientation of $\mathbf{S}$ and not on its length. From (3.13), by substitution of (3.3) and (3.4), the amplitude $C^\mu_{k_u}$ can be derived as (Lam, Beurskens & van Smaalen, 1992*a*)

$$C^\mu_{k_u}(\mathbf{S}) = \left[\sum_{i,j=1}^{3} S_i (\mathrm{U}^\mu_{k_u})_{ij} S_j \right]^{1/2}, \tag{3.14}$$

where $\mathsf{U}^{\mu}_{k_u}$ is a symmetric tensor that depends on the amplitudes and phases of the k_uth harmonic of the atomic displacement, through the definition of its components

$$(\mathsf{U}^{\mu}_{k_u})_{ij} = U^{\mu}_{k_u,i} U^{\mu}_{k_u,j} \cos(\alpha^{\mu}_{k_u,i} - \alpha^{\mu}_{k_u,j}). \tag{3.15}$$

Equation (3.14) clearly illustrates the anisotropic behavior of the displacive modulation. It can be shown that the displacive modulation simulates an anisotropic temperature effect (see Appendix *A*). For the benefit of this paper, however, an isotropic approach to the displacive modulation is needed. From (3.13), the amplitude $C^{\mu}_{k_u}$ can also be written as

$$C^{\mu}_{k_u}(\mathbf{S}) = 2s \left\{ (U^{\mu,c}_{k_u})^2 \cos^2[\delta^{\mu,c}_{k_u}(\mathbf{S})] + (U^{\mu,s}_{k_u})^2 \cos^2[\delta^{\mu,s}_{k_u}(\mathbf{S})] \right\}^{1/2}. \tag{3.16}$$

Here, $U^{\mu,c}_{k_u}$ and $U^{\mu,s}_{k_u}$ are the lengths of the vectors $\mathbf{U}^{\mu,c}_{k_u}$ and $\mathbf{U}^{\mu,s}_{k_u}$, respectively. The angles between the vectors $\mathbf{S}$ and $\mathbf{U}^{\mu,c}_{k_u}$ and between the vectors $\mathbf{S}$ and $\mathbf{U}^{\mu,s}_{k_u}$ are denoted by $\delta^{\mu,c}_{k_u}$ and $\delta^{\mu,s}_{k_u}$, respectively. Note that both angles only depend on the orientation of $\mathbf{S}$ and not on its length.

By substitution of (3.6) and (3.12) and by use of a relation between exponential functions and Bessel functions [equation (8.511-4) of Gradshteyn & Rhydzik (1980)], the integrand of (3.9) becomes

$$\sum_{k_p=-K_p}^{K_p} p^{\mu}_{k_p} \exp[2\pi i(k_p + m)\tau] \times$$

$$\prod_{k_u=1}^{K_u} \left(\sum_{m^{\mu}_{k_u}=-\infty}^{\infty} J_{m^{\mu}_{k_u}}[2\pi C^{\mu}_{k_u}(\mathbf{S})] \exp\{i m^{\mu}_{k_u}[\eta^{\mu}_{k_u}(\mathbf{S}) + \pi - 2\pi k_u \tau]\} \right), \tag{3.17}$$

where J_n is the nth-order Bessel function of the first kind. The multiple product with respect to k_u and the summation with respect to $m^{\mu}_{k_u}$ can be interchanged, which causes (3.17) to become

$$\sum_{k_p=-K_p}^{K_p} \sum_{m^{\mu}_1=-\infty}^{\infty} \cdots \sum_{m^{\mu}_{K_u}=-\infty}^{\infty} p^{\mu}_{k_p} \left\{ \prod_{k_u=1}^{K_u} J_{m^{\mu}_{k_u}}[2\pi C^{\mu}_{k_u}(\mathbf{S})] \right\} \times$$

$$\exp\left\{ i \sum_{k_u=1}^{K_u} m^{\mu}_{k_u}[\eta^{\mu}_{k_u}(\mathbf{S}) + \pi] \right\} \exp\left[2\pi i \left(k_p + m - \sum_{k_u=1}^{K_u} m^{\mu}_{k_u} k_u \right) \tau \right]. \tag{3.18}$$

With (3.18) for the integrand of (3.9), the integral with respect to τ can be evaluated. It follows that a term in the multiple summation of (3.18) only contributes to the integral if

the condition

$$\sum_{k_u=1}^{K_u} m_{k_u}^{\mu} k_u = k_p + m \tag{3.19}$$

is fulfilled. This leads to the following expression for the atomic modulation factor:

$$g^{\mu}(\mathbf{S},m) = \sum_{k_p=-K_p}^{K_p} \sum_{m_1^{\mu}=-\infty}^{\infty} \cdots \sum_{m_{K_u}^{\mu}=-\infty}^{\infty} p_{k_p}^{\mu} \left\{ \prod_{k_u=1}^{K_u} J_{m_{k_u}^{\mu}}[2\pi C_{k_u}^{\mu}(\mathbf{S})] \right\} \times$$

$$\exp\left\{ i \sum_{k_u=1}^{K_u} m_{k_u}^{\mu} [\eta_{k_u}^{\mu}(\mathbf{S}) + \pi] \right\}. \tag{3.20}$$

Note that (3.19) and (3.20) resemble similar expressions implicitly given by equation (7) of Petříček & Coppens (1988), where a more general case of displacive modulation is considered but where the effect of density modulation is not taken into account.

An expression for the intensity $|F|^2$ can be derived from (3.8), by substitution of (3.20) for the atomic modulation factor. Amongst other things, this expression depends on the average positions $\mathbf{r}_0^{\mu}$ and on the modulation parameters of the individual atoms. As for nonmodulated crystals (Wilson, 1942), the average of $|F|^2$ is calculated over a sufficiently large set of reflections in a narrow s interval. This set contains all diffraction vectors that have approximately the same length S and, therefore, have their end points within a thin shell of radius $S = 2s$ in reciprocal space. For a modulated crystal, the behavior of the intensity of main reflections is quite different from that of satellite reflections. Therefore, for each reflection order $|m|$, the average is calculated separately.‡ The average of $|F|^2$ over such a set of reflections is denoted by $\langle |F|^2 \rangle_{s,|m|}$. Note that the expression for $|F|^2$ contains a number of terms that will cancel when $\langle |F|^2 \rangle_{s,|m|}$ is evaluated. Which terms these are and under which conditions they cancel is briefly described below.

To evaluate the expression for $|F|^2$, the structure factor [(3.8)] is first multiplied by its complex conjugate. Some of the terms in the resulting multiple summation depend on a nonzero inter-atomic distance vector $\mathbf{r}_0^{\mu} - \mathbf{r}_0^{\nu}$, where μ and ν denote different atoms in the basic-structure unit cell. From the same assumptions as used by Wilson (1942), it can be

‡Let there be a large set of satellite reflections, with all satellites having their end points in a thin shell of radius S in reciprocal space and with the same reflection order $|m|$. This set can be divided into two other sets: one containing the $m < 0$ satellites and the other containing the $m > 0$ satellites. Because Friedel's law applies, a reflection in one of these two sets will always have a Friedel related reflection, having the same structure-factor amplitude, in the other set. This means that the average intensity is the same for both sets of reflections. Consequently, the average intensity is independent of the sign of the satellite index m.

shown that these terms will cancel when $\langle|F|^2\rangle_{s,|m|}$ is evaluated. Thus, in the expression for $|F|^2$ at hand, only the term $\sum_{\mu=1}^{N}|g^\mu f^\mu|^2$ has to be considered.

The next step involves the evaluation of $|g^\mu f^\mu|^2$ by substitution of (3.20) for the atomic modulation factor. In the resulting multiple summation, terms occur that contain a factor $\exp[i\sum_{k_u=1}^{K_u}(m_{k_u}^{\mu}-m_{k_u}^{\prime\mu})\eta_{k_u}^{\mu}(\mathbf{S})]$, with not all integer differences $m_{k_u}^{\mu}-m_{k_u}^{\prime\mu}$ equal to zero. From (3.13), with the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$ being nonzero and not parallel to one another for each pair (μ,k_u), it follows that, with the previously specified set of reflections, the numerical values of $\eta_{k_u}^{\mu}(\mathbf{S})$ (modulo 2π) are uniformly distributed throughout the interval $[0,2\pi]$.§ Consequently, these terms will also cancel when $\langle|F|^2\rangle_{s,|m|}$ is evaluated.

Herewith, the average intensity $\langle|F|^2\rangle_{s,|m|}$ can be written as

$$\left\langle|F|^2\right\rangle_{s,|m|}=\exp(-2Bs^2)\left\{\sum_{\mu=1}^{N}[f_0^{\mu}(s)]^2\right\}\Gamma(s;|m|). \tag{3.21}$$

The function Γ is written as a multiple summation of discrete averages,

$$\begin{aligned}\Gamma(s;|m|) \;=\; &\sum_{\mu=1}^{N}\sum_{k_p=-K_p}^{K_p}\sum_{m_1^{\mu}=-\infty}^{\infty}\cdots\sum_{m_{K_u}^{\mu}=-\infty}^{\infty}\\ &\frac{Z_\mu^2|p_{k_p}^{\mu}|^2}{\sigma}\left\langle\prod_{k_u=1}^{K_u}J_{m_{k_u}^{\mu}}^2[2\pi C_{k_u}^{\mu}(\mathbf{S})]\right\rangle_{s,|m|},\end{aligned} \tag{3.22}$$

where use has been made of (3.10) and (3.11). The first two factors in (3.21) make up the average intensity for nonmodulated crystals (Wilson, 1942) while the last factor (Γ) is the modification which describes the deviation from this average intensity caused by the displacive modulation and/or the density modulation. Note that the contribution of the displacive modulation to the average intensity is not only weighted by Z_μ^2 but, when density modulation occurs, also by a factor $|p_{k_p}^{\mu}|^2$. Thus, in the general case of displacive modulation and density modulation, mixing of different harmonics occurs in each term of (3.22).

In the limit of diminishing modulation (for all atoms μ; $U_{k_u,i}^{\mu}\to 0$ for all k_u and i, $P_0^{\mu}\to 1$ and $P_{|k_p|}^{\mu}\to 0$ for $k_p\neq 0$), equation (3.21) reduces to the average intensity for nonmodulated crystals. For main reflections ($m=0$), $\Gamma\to 1$ and (3.21) becomes identical to the average intensity for nonmodulated crystals. For satellite reflections ($m\neq 0$), $\Gamma\to 0$ and thus $\langle|F|^2\rangle_{s,|m|}\to 0$, *i.e.* the satellite reflections disappear.

§It is realized that this is not true for special cases of the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$, but such cases will not be considered here. Also note that, as in the conventional Wilson plot, atoms are supposed not to be on special positions.

3.4 Normalization of structure factors

For a proper evaluation of the average X-ray diffraction intensities, the symmetry of the crystal must be taken into account. It can be shown that its main effect is to enlarge the intensities of particular groups of reflections by a factor ϵ, the symmetry-enhancement factor, which can be defined as for nonmodulated crystals (Wilson, 1950; Giacovazzo, 1980; Lam, Beurskens & van Smaalen, 1993). One can then define the partially-normalized structure factor E_a by

$$E_a(\mathbf{S}) = F(\mathbf{S}) \left\{ \epsilon(\mathbf{S}) \sum_{\mu=1}^{N} [f_0^\mu(s)]^2 \right\}^{-1/2} \tag{3.23}$$

and, by use of (3.21), its mean square can be written as

$$\left\langle |E_a|^2 \right\rangle_{s,|m|} = \exp(-2Bs^2)\Gamma(s;|m|). \tag{3.24}$$

As the experimental intensities I are on a relative scale, a scale factor K is introduced and defined by

$$|F(\mathbf{S})|^2 = K^2 I(\mathbf{S}). \tag{3.25}$$

From (3.23), (3.24) and (3.25), the observed average of $|E_a|^2$ on a relative scale, denoted $G_o(s;|m|)$, can then be written as

$$G_o(s;|m|) = \left\langle I(\mathbf{S}) \left\{ \epsilon \sum_{\mu=1}^{N} [f_0^\mu(s)]^2 \right\}^{-1} \right\rangle_{s,|m|} \tag{3.26}$$

while the theoretical expectation value, denoted $G_c(s;|m|)$, is equal to

$$G_c(s;|m|) = K^{-2} \exp(-2Bs^2)\Gamma(s;|m|). \tag{3.27}$$

After reflections have been sorted, for each reflection order $|m|$, into suitable intervals of s, expressions (3.26) and (3.27) can be employed by a fitting procedure to estimate overall structural parameters (*e.g.* K, B and possibly modulation parameters) from average intensities.

Unfortunately, expression (3.22) for Γ is not very suitable for use by a fitting procedure. For nonmodulated crystals, the average X-ray diffraction intensity can be estimated without having any prior knowledge of the crystal structure, except for the contents of the unit cell (Wilson, 1942). Expression (3.22) not only depends on the contents of the basic-structure unit cell but also on the modulation parameters of individual atoms. Consequently, evaluation of the average intensity of an incommensurately modulated crystal also

requires knowledge of the complete atomic modulation functions (p^μ and $\mathbf{u}^\mu$). Therefore, to obtain an expression for the average intensity, which is suitable for use by a fitting procedure and which does not depend on modulation parameters of individual atoms, further approximation of Γ [(3.22)] and introduction of overall modulation amplitudes is necessary. When this has been done (see Sections 3.5 and 3.6), normalized structure factors can be defined by [(3.23), (3.24)]:

$$E(\mathbf{S}) = F(\mathbf{S}) \exp(Bs^2) \left\{ \epsilon(\mathbf{S}) \Gamma(s; |m|) \sum_{\mu=1}^{N} [f_0^\mu(s)]^2 \right\}^{-1/2} \tag{3.28}$$

3.5 A low-order approximation to Γ

As a first approximation to Γ, the discrete average is replaced by a continuous average, *i.e.* the last factor on the right-hand side of (3.22) is replaced by

$$\frac{1}{4\pi} \iint_\Omega \left\{ \prod_{k_u=1}^{K_u} J^2_{m^\mu_{k_u}} [2\pi C^\mu_{k_u}(\mathbf{S})] \right\} \mathrm{d}\Omega, \tag{3.29}$$

where the twofold integral with respect to Ω extends over all orientations of the diffraction vector, while s and $|m|$ do not change.

Furthermore, as in Lam, Beurskens & van Smaalen (1992*a*), it is assumed that the modulation amplitudes of the individual atoms are small. For this reason, all contributions to Γ as a result of integrals (3.29) will be neglected if the integrands are of order higher than 2 in the modulation amplitudes. Consequently, for all atoms μ, the multiple summation with respect to the integers $m^\mu_{k_u}$ in (3.22) can be restricted to terms of the following types:

type 1,

$$m^\mu_{k_u} = 0 \text{ for all } k_u; \tag{3.30}$$

type 2(*a*),

$$m^\mu_k = 1 \text{ and } m^\mu_{k_u} = 0 \text{ for } k_u \neq k; \tag{3.31}$$

type 2(*b*),

$$m^\mu_k = -1 \text{ and } m^\mu_{k_u} = 0 \text{ for } k_u \neq k. \tag{3.32}$$

Of course, each of the conditions (3.30), (3.31) and (3.32) restricts the summation with respect to k_p as well. For each of these terms, the contribution to Γ is evaluated as follows.

For terms of type 1, combination of conditions (3.19) and (3.30) results in the extra condition $k_p = -m$, *i.e.* the summation with respect to k_p in (3.22) no longer exists for this case. As a result, a nonzero contribution to Γ for terms of type 1 is only possible if the condition $-K_p \leq m \leq K_p$ is fulfilled. As will be discussed later, K_p can always be chosen as to meet this condition (see Section 3.7). The contribution to Γ can then be written, using (3.29), as

$$\sum_{\mu=1}^{N} \frac{Z_\mu^2 |p_m^\mu|^2}{4\pi\sigma} \iint_\Omega \left\{ \prod_{k_u=1}^{K_u} J_0^2[2\pi C_{k_u}^\mu(\mathbf{S})] \right\} \mathrm{d}\Omega. \tag{3.33}$$

On the assumption that the amplitudes $C_{k_u}^\mu$ are small, the multiple product in (3.33) can be approximated using the series expansion for Bessel functions [equation (8.440) of Gradshteyn & Ryzhik (1980)] and disregarding all terms of order higher than 2 in the amplitudes $C_{k_u}^\mu$. Subsequent substitution of (3.16) for $C_{k_u}^\mu$ results in the following expression for the integrand of (3.33):

$$1 - 8\pi^2 s^2 \sum_{k_u=1}^{K_u} \left\{ (U_{k_u}^{\mu,c})^2 \cos^2[\delta_{k_u}^{\mu,c}(\mathbf{S})] + (U_{k_u}^{\mu,s})^2 \cos^2[\delta_{k_u}^{\mu,s}(\mathbf{S})] \right\}. \tag{3.34}$$

Note that each of the terms in (3.34) can be integrated independently. Thus, the angles $\delta_{k_u}^{\mu,c}$ and $\delta_{k_u}^{\mu,s}$ can be replaced by a single integration variable δ and $\mathrm{d}\Omega = \sin(\delta)\,\mathrm{d}\delta\,\mathrm{d}\xi$, where δ and ξ are polar angles, with $\delta \in [0, \pi]$ and $\xi \in [0, 2\pi]$, describing the orientation of the diffraction vector. Expression (3.34) can then be replaced by

$$1 - 8\pi^2 s^2 \left[\sum_{k_u=1}^{K_u} (U_{k_u}^\mu)^2 \right] \cos^2(\delta), \tag{3.35}$$

where the atomic modulation amplitudes $U_{k_u}^\mu$ are given by

$$U_{k_u}^\mu = \left[(U_{k_u}^{\mu,c})^2 + (U_{k_u}^{\mu,s})^2 \right]^{1/2}. \tag{3.36}$$

By substitution of (3.35) for the integrand and by use of the transformation $x = \cos(\delta)$, expression (3.33) becomes

$$P_m^2 \int_0^1 \{1 - [4\pi s(V_m/P_m)x]^2/2\}\,\mathrm{d}x, \tag{3.37}$$

with overall modulation amplitudes defined by

$$P_{k_p} = \left(\frac{1}{\sigma} \sum_{\mu=1}^{N} Z_\mu^2 |p_{k_p}^\mu|^2 \right)^{1/2}, \tag{3.38}$$

$$V_{k_p} = \left(\sum_{k_u=1}^{K_u} V_{k_p,k_u}^2 \right)^{1/2} \tag{3.39}$$

and

$$V_{k_p,k_u} = \left[\frac{1}{\sigma} \sum_{\mu=1}^{N} Z_\mu^2 |p_{k_p}^\mu|^2 (U_{k_u}^\mu)^2 \right]^{1/2} \tag{3.40}$$

Note that the amplitudes V_{k_p,k_u} are a mixture of the modulation amplitudes of the $|k_p|$th harmonic of the density modulation and those of the k_uth harmonic of the displacive modulation.

Expression (3.37) is not a very good approximation to (3.33). Especially at larger s values and larger displacive modulations, the integrand of (3.37) may even become negative. In contrast, the integrand of (3.33) is positive or zero. To improve the behavior of the present approximation, expression (3.37) is written as

$$P_m^2 \prod_{k_u=1}^{K_u} \int_0^1 \{1 - [4\pi s(V_{m,k_u}/P_m)x]^2/2\} \, \mathrm{d}x, \tag{3.41}$$

which is correct up to second order in the amplitudes of the displacive modulation. Using the series expansion for Bessel functions, the integrand of (3.41) can be replaced by

$$J_0^2[4\pi s(V_{m,k_u}/P_m)x]. \tag{3.42}$$

From a strictly mathematical point of view, the replacement of a truncated series expansion by a special function is, in general, not a unique operation. Of course, the main reason to use (3.42) for the integrand of (3.41) is that squared Bessel functions are also involved in expression (3.33). In addition, squared Bessel functions show a more desirable behavior at larger values of their arguments. This is in contrast to, for example, approximations based on exponential functions. Furthermore, for a special case of displacive modulation, it can be shown that, for main reflections ($m = 0$), expression (3.33) can be evaluated to correspond exactly to equation (12) of Lam, Beurskens & van Smaalen (1992*a*). This also suggests the use of Bessel functions for incorporating effects of higher-order terms in the series expansion. By use of (3.42) for the integrand of (3.41),¶ the contribution to Γ for

¶Instead of the integrand of (3.41), one can also replace the integrand of (3.37) by a squared Bessel function. Expression (3.44) can then be replaced by

$$P_m^2 Z(s; 0, V_m/P_m). \tag{3.43}$$

Although this is a less complicated expression than (3.44), it has a serious disadvantage. For crystals with large displacive modulations, the overall modulation amplitudes V_{k_p} will be considerably larger than

terms of type 1 can finally be written as

$$P_m^2 \prod_{k_u=1}^{K_u} Z(s;0,V_{m,k_u}/P_m), \tag{3.44}$$

where the function Z is defined by [equation (12) of Lam, Beurskens & van Smaalen (1992*a*)]

$$Z(s;n,u) = \int_0^1 J_n^2(4\pi s u x)\,\mathrm{d}x. \tag{3.45}$$

For terms of type 2(*a*), combination of conditions (3.19) and (3.31) results in the extra condition $k = k_p + m$. Therefore, the summation with respect to k_p in (3.22) is now restricted to those terms which fulfil the condition $1 \le k_p + m \le K_u$. The contribution to Γ can then be written, using (3.29), as

$$\sum_{\mu=1}^{N} \sum_{\substack{k_p=-K_p \\ 1\le k_p+m\le K_u}}^{K_p} \frac{Z_\mu^2 |p_{k_p}^\mu|^2}{4\pi\sigma} \iint_\Omega \left\{ J_1^2[2\pi C_{k_p+m}^\mu(\mathbf{S})] \prod_{\substack{k_u=1 \\ k_u\ne k_p+m}}^{K_u} J_0^2[2\pi C_{k_u}^\mu(\mathbf{S})] \right\} \mathrm{d}\Omega. \tag{3.46}$$

Going through the same procedure as used for terms of type 1, this expression can be approximated by

$$\sum_{\substack{k_p=-K_p \\ 1\le k_p+m\le K_u}}^{K_p} P_{k_p}^2 \int_0^1 \{[4\pi s(V_{k_p,k_p+m}/P_{k_p})x]^2/4\}\,\mathrm{d}x, \tag{3.47}$$

where the overall modulation amplitudes P_{k_p} and V_{k_p,k_p+m} are given by (3.38) and (3.40), respectively. Note that the integrand of (3.47) only contains a contribution from the factor J_1^2 in (3.46). In the present low-order approximation, neglect of the higher-order terms has effectively the same result as if all factors J_0^2 in (3.46) had been replaced by 1.

By use of the series expansion for Bessel functions, the factor between braces in the integrand of (3.47) can be replaced by a factor J_1^2. The contribution to Γ for terms of type 2(*a*) can then finally be written as

$$\sum_{\substack{k_p=-K_p \\ 1\le k_p+m\le K_u}}^{K_p} P_{k_p}^2 Z(s;1,V_{k_p,k_p+m}/P_{k_p}), \tag{3.48}$$

the amplitudes V_{k_p,k_u}. However, the present approximations are based on small modulation amplitudes. Therefore, expression (3.44) is expected to be a better approximation. Numerical tests show that this is true indeed. Especially for main reflections, where Γ is mainly determined by the contribution from terms of type 1, and at higher s values, severe deviation from the true intensity distribution occurred when (3.43) was used to estimate the X-ray diffraction intensities.

with the function Z given by (3.45).

For terms of type 2(b), conditions (3.19) and (3.32) lead to the extra condition $k = -(k_p + m)$ and the summation with respect to k_p in (3.22) is restricted to those terms which fulfil the condition $1 \leq -(k_p + m) \leq K_u$. Because the contribution to Γ for these terms can be derived in exactly the same way as described for terms of type 2(a), it can also be obtained from (3.48) by replacement of every occurrence of $k_p + m$ by $-(k_p + m)$.

As a further simplification, one can assume that, for the $|k_p|$th harmonic of the density modulation, the amplitudes $|p^{\mu}_{k_p}|$ are approximately the same for all atoms. One can then use the approximation

$$\frac{V_{k_p,k_u}}{P_{k_p}} \simeq U_{k_u} = \left[\frac{1}{\sigma}\sum_{\mu=1}^{N} Z_{\mu}^2 (U^{\mu}_{k_u})^2\right]^{1/2} \tag{3.49}$$

While, for given K_p and K_u, expressions (3.44) and (3.48) require a total number of $(K_p + 1)(K_u + 1)$ overall modulation amplitudes, with approximation (3.49) only $K_p + 1 + K_u$ amplitudes are needed. This reduction of the total number of overall modulation amplitudes is very important for the development of a fitting procedure. It will not only improve the convergence of the procedure, but the fit parameters can also be obtained more accurately. In fact, preliminary tests showed that without (3.49), a successful fitting procedure could not be developed because of dependencies between the fit parameters, as will be discussed in Section 3.7. Also note that the new overall modulation amplitudes U_{k_u} only depend on the displacive modulation, whereas the amplitudes V_{k_p,k_u} also depend on the density modulation. This means that, with (3.49), density modulation and displacive modulation have been 'decoupled', *i.e.* each type of modulation now has its own overall modulation amplitudes. This will make it easier to interpret the parameters obtained from the fitting procedure.

With the expressions [(3.44), (3.48)] for the terms of type 1 and 2[(a) and (b)], using approximation (3.49), and with zero for other terms, expression (3.22) leads to the following result for Γ:

$$\Gamma(s;m) = P_m^2 \prod_{k_u=1}^{K_u} Z(s;0,U_{k_u}) + \sum_{\substack{k_p=-K_p \\ 1\leq|k_p+m|\leq K_u}}^{K_p} P_{k_p}^2 Z(s;1,U_{|k_p+m|}). \tag{3.50}$$

To show that approximation (3.50) is independent of the sign of the satellite index m, one should note that from (3.7) it follows that $|p^{\mu}_{k_p}| = |p^{\mu}_{-k_p}|$ for all μ and k_p. Consequently,

the amplitudes P_{k_p} are independent of the sign of k_p. As a direct result, the first term of (3.50) is independent of the sign of m. Further, the second term of (3.50) does not change if both m and k_p are reversed in sign. Hence, Γ [(3.50)] is independent of the sign of the satellite index.

Before discussing which overall modulation amplitudes can be estimated from a fitting procedure employing (3.50), two special cases for Γ will be considered first.

3.6 Special cases for Γ

While (3.50) describes the effect of combined density and displacive modulations on the average X-ray diffraction intensities, one can also consider crystals where only one of these two types of modulations occurs.

For crystals with only density modulation [$U^{\mu}_{k_u,i} = 0$ for all μ, k_u and i; see equation (3.1)], one can easily show that $U_{k_u} = 0$, so that (3.50) reduces to

$$\Gamma(s;m) = P_m^2 \tag{3.51}$$

(assuming that K_p is large enough; see Section 3.7). It follows that, for each reflection order $|m|$, $G_c(s;|m|)$ has the same functional form as the corresponding expression for nonmodulated crystals (Wilson, 1942). This means that, for this special case, average intensities can be estimated from a Wilson plot which can be made separately for each reflection order (although this is not a recommended procedure).

If only displacive modulation occurs [for all atoms μ, $P_0^{\mu} \neq 0$ and $P^{\mu}_{|k_p|} = 0$ for $k_p \neq 0$; see equation (3.5)], it follows that $P_0 \neq 0$ and $P_{k_p} = 0$ for $k_p \neq 0$. Consequently, equation (3.50) reduces to

$$\Gamma(s;m) = \begin{cases} P_0^2 \prod_{k_u=1}^{K_u} Z(s;0,U_{k_u}) & (m=0) \\ \\ P_0^2 Z(s;1,U_{|m|}) & (m \neq 0) \end{cases} \tag{3.52}$$

(assuming that K_u is large enough; see Section 3.7). For small displacive modulations, $\prod_{k_u=1}^{K_u} Z(s;0,U_{k_u})$ can be approximated by $\exp(-8\pi^2 s^2 U^2/3)$, where U is defined by equation (3.58) of Appendix A. This means that $\Gamma(s;0)$ resembles an isotropic temperature factor, causing $G_c(s;0)$ to have the same functional form as the corresponding expression for nonmodulated crystals. Hence, for this special case, only the average intensities of main reflections can be used in a conventional Wilson plot. For satellite reflections, this is not possible because $Z(s;1,U_{|m|})$ first increases with increasing s and then decreases,

which is not the behavior of a temperature factor. (See Appendix A for a relation between temperature parameters and displacive modulation.) Note that if the displacive modulation only contains a first-order harmonic ($K_u = 1$), equation (3.52) combined with (3.21) corresponds to equation (13) of Lam, Beurskens & van Smaalen (1992*a*).

3.7 Estimating overall modulation amplitudes

The atomic modulation functions ($\mathbf{u}^\mu$ and p^μ) are represented by truncated Fourier series [(3.1) and (3.5)], whereas the true series expansions of these functions may contain an infinite number of harmonics, which also implies an infinite number of modulation amplitudes. However, a fitting procedure, employing either (3.50), (3.51) or (3.52), can only estimate a few modulation parameters from the collected intensity data. This also limits the number of terms of the truncated Fourier series, given by K_p and K_u, and gives an impression of the number of harmonics that can be used to develop a model of the incommensurately modulated structure.

To estimate overall modulation amplitudes from a fitting procedure, it is assumed that, for each reflection order $|m|$, up to a maximum order $m_{\max}$, the data set contains enough reflections to draw a plot of $\ln G_o(s;|m|)$ *versus* s^2. For modulated crystals, this plot may be considered as the analog of the Wilson plot for nonmodulated crystals.

One problem is that a fitting procedure will not be able to separate the scale factor K from the amplitudes P_{k_u}. When (3.27) is combined with either (3.50), (3.51) or (3.52), the scale factor always appears in the factors P_{k_u}/K. To solve this problem, one can either fix the value of the scale factor or the value of the amplitude P_0. A reasonable estimate for the scale factor can be obtained from a conventional Wilson plot applied only to the intensities of the main reflections. On the other hand, an *a priori* chemical analysis of the contents of the basic-structure unit cell may result in an estimate for the overall amplitude P_0. In the following, it is assumed that a reasonable estimate for the scale factor is available, which is kept fixed. Estimates for the overall modulation amplitudes can then be obtained as follows.

For the special cases mentioned in Section 3.6, the situation is fairly simple. If only density modulation occurs, $K_u \equiv 0$ and Γ given by (3.51), extrapolation of the plots towards $s = 0$ results in estimates for amplitudes P_{k_p} with $0 \leq |k_p| \leq m_{\max}$. The slope of each plot gives an estimate for the isotropic temperature parameter B. [With expression (3.51) for Γ, the plots must be straight lines, parallel to one another.] Note that the Fourier series for the density modulation functions has to be restricted to $K_p = m_{\max}$.

For the case where only displacive modulation occurs, $K_p \equiv 0$ and Γ is given by (3.52). It is evident that B and U cannot be obtained separately from a fitting procedure if only main reflections are involved. The reason is that, for main reflections, the displacive modulation simulates a temperature effect which adds to the true temperature parameter B, leading to the (pseudo) temperature parameter $B_a = B + 4\pi^2 U^2/3$ of the average structure (see Section 3.6 and Appendix A). However, the dependency of $Z(s;0,u)$ on s is entirely different from that of $Z(s;1,u)$. One can therefore use main reflections together with satellites, in a single fitting procedure, to separate all amplitudes U_{k_u} with $1 \leq k_u \leq m_{\max}$ from the temperature parameter B [Lam, Beurskens & van Smaalen (1992*a*)]. The Fourier series for the displacive modulation functions can then be restricted to $K_u = m_{\max}$. Amplitudes U_{k_u} corresponding to higher-order harmonics ($k_u > m_{\max}$) cannot be separated from the temperature parameter B and may be given a zero value. The amplitude P_0 can be determined by extrapolation of the intensity distribution for the main reflections towards $s = 0$.

For the general case, with Γ given by (3.50), extrapolation towards $s = 0$ results in estimates for amplitudes P_{k_p} with $0 \leq |k_p| \leq m_{\max}$. To find out which of the amplitudes U_{k_u} can be determined from a fitting procedure, one should remember that (3.50) is derived using the assumption of small displacive modulations and series are only expanded up to second order in the amplitudes of the displacive modulation. A similar series expansion of (3.50), up to second order in the amplitudes U_{k_u}, would lead to a first-order polynomial in s^2. Consequently, in the present low-order approximation, the $m_{\max} + 1$ intensity distributions allow at most $2(m_{\max}+1)$ fit parameters. Because the temperature parameter B and the amplitudes P_{k_p} already require $m_{\max} + 2$ fit parameters, there can be at most $m_{\max}$ fit parameters associated with the amplitudes U_{k_u}. On the assumption that the lower-order harmonics are the most important ones, one can only estimate amplitudes U_{k_u} with $1 \leq k_u \leq m_{\max}$. The Fourier series for the displacive modulation can then be restricted to $K_u = m_{\max}$.

Note that in practical situations, *e.g.* the refinement of a real structure with an incommensurate one-dimensional modulation, the Fourier series for the modulation functions are usually restricted to $K_p = K_u = m_{\max}$, because if satellite reflections with $|m| > m_{\max}$ are too weak to be observed, one may assume that harmonics with $|k_p| > m_{\max}$ or $k_u > m_{\max}$ are insignificant. However, this is not always the case.

One should be aware that (3.50), (3.51) and (3.52) are only approximations to (3.22). Therefore, the rules given above should not be applied blindly. For example, consider a crystal where only displacive modulation occurs and assume that the atomic modulation functions only contain first-order harmonics, *e.g.* sine waves. If the amplitudes of the

atomic displacements are large enough, nonzero average X-ray diffraction intensities may be obtained not only for main reflections and first-order satellites but also for second-order satellites. Estimation of overall modulation amplitudes, by use of expression (3.52) for Γ, will then result in nonzero values for the amplitudes U_1 and U_2. However, from the atomic modulation functions, it follows that $U_{k_u} \equiv 0$ for $k_u > 1$. The discrepancy lies in the fact that in the derivation of (3.50), only a few low-order terms in the multiple summation of (3.22) have been considered [terms of type 1 and 2(*a* and *b*)]. But the first-order harmonics also contribute to second- and higher-order reflections through the higher-order terms in the multiple summation of (3.22). This discrepancy especially occurs for large atomic displacements.

On the other hand, consider a crystal with large anharmonic displacive modulations, where higher-order harmonics are very important, *e.g.* a 'saw-tooth' modulation. Special structural effects which also occur for nonmodulated crystals, *e.g.* molecules with a noncrystallographic centre of symmetry, and special types of modulation, *e.g.* 'rigid-body' modulation, may result in an excess of weak X-ray diffraction intensities (Lam, Beurskens & van Smaalen, 1993). Consequently, it may not be possible to measure satellite reflections of order higher than 1 because these reflections are to weak to become observed. One may then easily conclude from the available intensity distributions that higher-order harmonics are not important.

Note that for crystals with only density modulation, the rule described above is correct because the $|k_p|$th-order harmonics only contribute to reflections of order $|k_p|$.

3.8 Numerical evaluation

The validity of approximation (3.50) for Γ has been tested by calculating intensity distributions from the simulated X-ray diffraction data of several model structures with different incommensurate one-dimensional modulations. As for nonmodulated crystals, the assumptions underlying the approximations require a structure with many symmetry-independent equal atoms that are randomly distributed throughout the basic-structure unit cell. Here, also, a random distribution of the components of the atomic modulation functions is required. The model structures were devised as to fulfil these requirements as closely as possible. As a first test for the theory, expectation values for average X-ray diffraction intensities were estimated using overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural model. For a subsequent test, overall modulation amplitudes obtained from a fitting procedure were used.

Table 3.1. Model structure characteristics.

Minimum and maximum values for the atomic modulation amplitudes $P^{\mu}_{|k_p|}$ $(0 \leq |k_p| \leq K_p = 2)$ and $U^{\mu}_{k_u}$ $(1 \leq k_u \leq K_u = 2)$ of the following model structures: structure P with displacive modulation; structure D with density modulation; structure DP with density modulation and displacive modulation (see text for explanation). The overall modulation amplitudes corresponding to the atomic modulation amplitudes are given in Table 3.2.

Model structure	P^{μ}_0 min./max.	P^{μ}_1 min./max.	P^{μ}_2 min./max.	U^{μ}_1 (Å) min./max.	U^{μ}_2 (Å) min./max.
P	1/1	0/0	0/0	0.095/0.256	0.019/0.123
D	0.781/0.979	0.401/0.591	0.147/0.337	0/0	0/0
DP	0.781/0.979	0.401/0.591	0.147/0.337	0.095/0.256	0.019/0.123

Characteristics of the model structures together with details of all atomic modulations are given in Table 3.1. All model structures (denoted P, D and DP) created have superspace group $P\bar{1}(q_1, q_2, q_3)\bar{1}$, with a realistic modulation wave vector. The basic-structure unit cell has realistic cell dimensions and contains 50 carbon atoms, with the symmetry-independent atoms randomly distributed throughout the cell and not occupying any special positions. The model structures come with different types of modulation: structure P with displacive modulation, structure D with density modulation, and structure DP with a combination of density modulation and displacive modulation. The maximum numbers of harmonics contributing to the atomic modulation functions [(3.1) and (3.5)] are restricted to $K_p = K_u = 2$. Amplitudes and phases of the atomic modulation functions where chosen at random, but the atomic modulation amplitudes $P^{\mu}_{|k_p|}$ and $U^{\mu}_{k_u}$ [(3.36)] fluctuate within reasonable limits around the overall modulation amplitudes P_{k_p} and U_{k_u}, given by (3.38) and (3.49), respectively. For an atom of structure DP, the modulation was obtained by combining the displacive modulation of the corresponding atom in structure P with the density modulation of the same atom in structure D. Furthermore, for each reflection order $|m|$, reflections of structure D have approximately the same average intensity as reflections of structure P. Consequently, structure DP is not dominated by a particular type of modulation. Overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural model are given in lines m of Table 3.2. For all model structures, structure factors were calculated (Yamamoto, 1985) for main reflections and first- and second-order satellites ($m_{\max} = 2$), up to $s = 1$ Å^{-1}, using $K = 1$ and $B = 2$ Å^2. (These calculated reflection intensities are denoted 'reflection data'.)

For each model structure, the intensity distributions (3.26) were obtained from the reflection data as follows. First, suitable s intervals were created by dividing reciprocal

Table 3.2. Overall modulation amplitudes.

For each model structure, line m contains the values of the overall isotropic temperature parameter B and the overall modulation amplitudes P_{k_p} $(0 \leq k_p \leq K_p = 2)$ and U_{k_u} $(1 \leq k_u \leq K_u = 2)$ calculated directly from the atomic parameters of the structural model. Similarly, line f contains the values of the same overall parameters, but now they are obtained from a fitting procedure employing (3.26) and (3.27) with (3.50). For comparison, line W contains the values of the parameters B and P_0 obtained from a conventional Wilson plot applied only to the intensities of the main reflections.

Model structure		B (Å^2)	P_0	P_1	P_2	U_1 (Å)	U_2 (Å)
P	*m*	2	1	0	0	0.200	0.080
	f	2.00	0.999	0.001	0.000	0.195	0.081
	W	2.45	0.965				
D	*m*	2	0.900	0.250	0.125	0	0
	f	1.99	0.897	0.248	0.124	0.000	0.000
	W	1.98	0.895				
DP	*m*	2	0.900	0.250	0.125	0.200	0.080
	f	2.01	0.914	0.243	0.123	0.199	0.084
	W	2.41	0.867				

space into spherical shells of equal volume. Then, for each reflection order $|m|$, reflections were partially normalized and sorted into these intervals. Thus, each interval contains approximately the same number of reflections. In a progressive averaging procedure, each interval was combined with its two neighboring intervals. Finally, for each reflection order, the resulting data points were plotted as graphs of $\ln G_o(s;|m|)$ *versus* s^2.

As a first test, for each reflection order, expectation values G_c were estimated by use of equation (3.27), combined with expression (3.50) for Γ, and compared with the intensity distributions (3.26) obtained from the reflection data. Here, Γ was evaluated using overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural model (see lines m of Table 3.2). Figures 3.1(a), (c) and (e) show that, for all model structures, the true intensity distributions are accurately reproduced, although a small deviation at higher s values can be observed for the intensity distribution of the second-order satellites of structure *DP*.

As a next step, for each model structure, the modulation parameters were estimated by use of a fitting procedure employing (3.26), (3.27) and (3.50). Fitting was done with the Marquardt nonlinear least-squares method (Kowalik & Osborne, 1968; Bevington, 1969). With the highest reflection order $m_{\max}$ equal to 2, the following fit parameters were used: the overall isotropic temperature parameter B and the overall modulation amplitudes P_{k_p} $(0 \leq k_p \leq K_p = 2)$ and U_{k_u} $(1 \leq k_u \leq K_u = 2)$. The scale factor K was fixed to have

the value 1 (see discussion in Section 3.7). Starting values for B and P_0 were obtained from a conventional Wilson plot applied only to the intensities of the main reflections. (The amplitude P_0 was assigned the value of K_w^{-1}, where K_w is the scale factor of the Wilson plot.) The starting values for the amplitudes P_1 and P_2 were set to 0.001 while the amplitudes U_1 and U_2 were assigned starting values of 0.001 Å. The fitting procedure minimalized the function

$$\chi_r^2 = \frac{\sum_{i=1}^{n_o} w_i (y_i^o - y_i^c)^2}{n_o - n_p}, \tag{3.53}$$

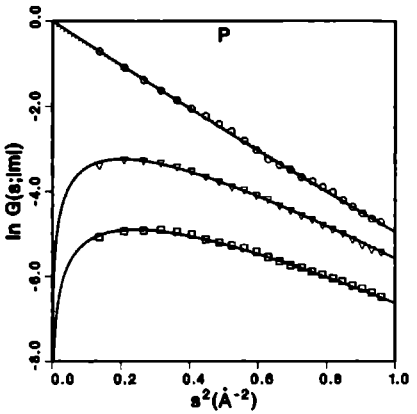
where, for each model structure, the summation with respect to i counts the number of data points up to a total number of n_o data points in all intensity distributions together, n_p is the number of fit parameters and w_i is a weight factor that counts the total number of reflections in each s interval. Further, y_i^o is equal to $\ln G_o(s;|m|)$ calculated from the reflection data and y_i^c, which is a function of the fit parameters, is equal to $\ln G_c(s;|m|)$. Refinement of the fit parameters was stopped when the decrease of χ_r^2 became less than 0.1% of the previous χ_r^2 value.

For all model structures, the parameters obtained from the fitting procedure (see lines *f* of Table 3.2) are in good agreement with the parameters *a priori* calculated from the atomic parameters of the structural model (see lines *m* of Table 3.2). The starting parameters for B and P_0, obtained from the Wilson plot, are given by lines *W* of Table 3.2. Note that for structures *P* and *DP*, where displacive modulation occurs, the B values obtained from the Wilson plot are significantly larger than the B values obtained from the fitting procedure. This is caused by the large correlation between displacive modulation and thermal motion (see Appendix *A*). For structure *D*, where only density modulation occurs, the values of the parameters B and P_0 obtained from the Wilson plot are in good agreement with the values obtained from the fitting procedure.

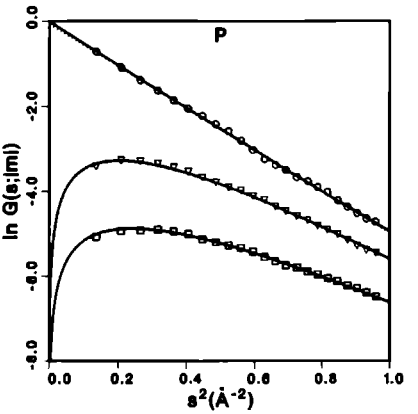
Figures 3.1(*b*), (*d*) and (*f*) show that, for all model structures, the intensity distributions (3.26) calculated from the simulated reflection data are accurately reproduced by the intensity distributions estimated from the parameters obtained by the fitting procedure. Also note that the Wilson plot, used to estimate the starting values for B and P_0, indicated by a dotted line in each figure, coincides largely with the intensity distribution estimated for the main reflections.

The convergence of the fitting procedure turned out to be reasonably fast.‖ For structure *P* (displacive modulation), approximately three times as many cycles were needed before the stopping criterion was fulfilled. This slower convergence was probably caused

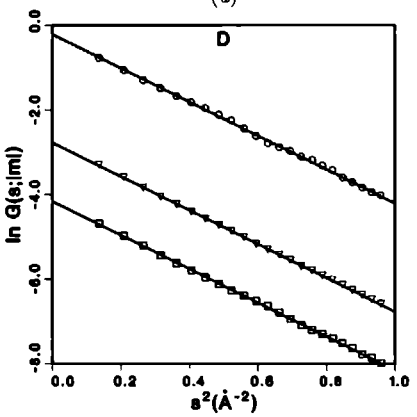
‖Less than a few minutes on a PC with a 80486 processor.


P
ln G(s;|m|)
s²(Å⁻²)

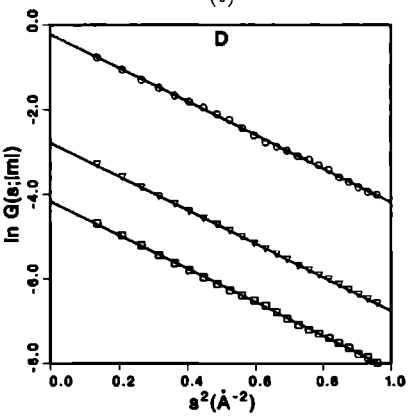
(a)


P
ln G(s;|m|)
s²(Å⁻²)

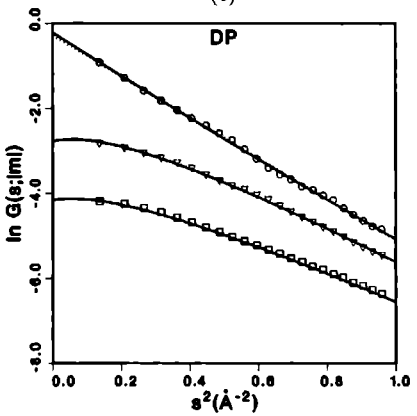
(b)


D
ln G(s;|m|)
s²(Å⁻²)

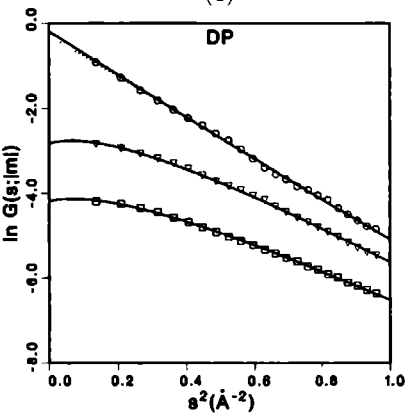
(c)


D
ln G(s;|m|)
s²(Å⁻²)

(d)


DP
ln G(s;|m|)
s²(Å⁻²)

(e)


DP
ln G(s;|m|)
s²(Å⁻²)

(f)

◁

Figure 3.1. Natural logarithm of the partially-normalized average intensity $G_o(s;|m|)$, as a function of s^2, for main reflections (circles), $|m| = 1$ satellites (triangles) and $|m| = 2$ satellites (squares). The dotted lines are conventional Wilson plots applied only to the intensities of the main reflections. The solid lines represent $G_c(s;|m|)$ calculated by use of equation (3.27), combined with expression (3.50) for Γ and with overall modulation amplitudes which are either calculated directly from the structural model or obtained from the fitting procedure: (*a*) structure *P* with amplitudes from the model; (*b*) structure *P* with amplitudes from the fit; (*c*) structure *D* with amplitudes from the model; (*d*) structure *D* with amplitudes from the fit; (*e*) structure *DP* with amplitudes from the model; (*f*) structure *DP* with amplitudes from the fit.

by the amplitudes P_1 and P_2 which behaved somewhat unstable during the refinement process. This is explained as follows. As mentioned earlier, each amplitude P_{k_p} ($k_p \neq 0$) is estimated by extrapolation of the intensity distribution for the $|k_p|$th-order satellites towards $s = 0$. This is also seen from equation (3.50) for Γ, where the first term, which is important at the lower s values, depends heavily on the amplitudes P_{k_p} ($k_p \neq 0$), whereas the second term, which is important at the higher s values, only weakly depends on these amplitudes. However, there are some problems regarding this extrapolation. First of all, the s intervals at lower s values are much larger than those at higher s values, so there are few data points near $s = 0$. Of course, one can use smaller intervals, but this does not solve the problem because the weight of the data points, which is the number of reflections in each interval, must be adjusted accordingly. In addition, as for nonmodulated crystals, one of the assumptions that lead to equation (3.50) is not valid for $s \simeq 0$ (Wilson, 1949). Thus, the few data points near $s = 0$ are unreliable and should be excluded from the fitting procedure. Secondly, for crystals where only displacive modulation occurs, the intensity distributions for the satellite reflections show asymptotic behavior at $s = 0$, *i.e.* $\ln G_c(s,|m|) \rightarrow -\infty$ for $s \rightarrow 0$ and $m \neq 0$ [see Figures 3.1(*a*) and (*b*)]. For these two reasons, determination of the amplitudes P_{k_p} ($k_p \neq 0$), by extrapolation of the intensity distributions for the satellite reflections towards $s = 0$, will be less straightforward. In fact, the refinement of these amplitudes depends heavily on the second term of (3.50) which only weakly depends on these amplitudes. As a result, convergence of the amplitudes P_{k_p} ($k_p \neq 0$) will be slower but the values obtained from the fitting procedure will be correct, as is seen in Table 3.2. This slower convergence will occur for any crystal with displacive modulation being the dominant type of modulation.

3.9 Concluding remarks

A theoretical expression is derived for the average X-ray diffraction intensity, as function of $(\sin\theta)/\lambda$, of main reflections and low-order satellite reflections of crystals with an incommensurate one-dimensional modulation. The atomic modulation functions for displacive and density modulations contain harmonics up to any order. The modulation of individual atoms is taken into account by the introduction of overall modulation amplitudes. The theoretical average intensity is equal to the average X-ray diffraction intensity of nonmodulated crystals (Wilson, 1942), multiplied by a modification factor that depends on $(\sin\theta)/\lambda$, the reflection order $|m|$ and the overall modulation amplitudes.

Tests, performed on three idealized model structures show that the theoretical intensity distributions (3.27), employing approximation (3.50), are in excellent agreement with the simulated intensity distributions. A fitting procedure is presented which enables the estimation of the scale factor, the overall isotropic temperature parameter, and the overall modulation parameters from the experimental intensity distributions (3.26). The estimated parameters again are in excellent agreement with the parameters calculated directly from the structural parameters [(3.38, 3.49)].

As is expected for the present idealized test structures, the theoretical intensity distributions evaluated by use of estimated parameters compare slightly better with the simulated intensity distributions than when they are evaluated by use of calculated parameters. This is more prominently observed for the second-order satellites.

The values of the overall modulation amplitudes estimated from the fitting procedure can be used to obtain information about the type of modulation and the importance of the various harmonics involved in the atomic modulation functions.

The first applications of direct methods to incommensurately modulated structures employed $|F|$ values instead of normalized structure factors (Hao, Liu & Fan, 1987; Xiang, Fan, Wu & Li, 1990), as a definition for the latter was not yet available. Recently, preliminary definitions for normalized structure factors have been proposed (Lam, Beurskens & van Smaalen, 1992*a*, 1992*b*, 1993), with atomic modulation functions that contain only a first-order harmonic. A more general definition for normalized structure factors of crystals with an incommensurate one-dimensional modulation has now been given in equation (3.28). These normalized structure factors can be used for the computerization of various direct-methods procedures. Experiments regarding the use of these normalized structure factors in the triplet phase relationship and the tangent formula (Karle & Karle, 1966) are in progress (Lam *et al.*, 1994).

In situations where the displacive modulation gives large anisotropic effects in recipro-

cal space, equation (3.14) may be the basis for a more accurate definition of normalized structure factors for crystals with an incommensurate one-dimensional modulation

Acknowledgements

The authors thank A. Janner (University of Nijmegen) for many stimulating discussions. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO).

Appendix A

For crystals with displacive modulation, it is well known that the temperature parameters of an atom in the average structure, (*i.e.* the structure obtained from main reflections only), are usually larger than those of the same atom in the basic structure because the displacive modulation simulates a temperature effect (Pérez-Mato, Madariaga & Tello, 1986). The relation between these temperature parameters and the displacive modulation of the atom is shown as follows. The correction to the atomic scattering factor as a result of the anisotropic thermal vibration of an atom is given by

$$\exp\left[-\frac{1}{4}\sum_{i,j=1}^{3}(\mathsf{B}^{\mu})_{ij}S_iS_ja_i^*a_j^*\right], \tag{3.54}$$

where $(\mathsf{B}^{\mu})_{ij}$ is the ijth component of the temperature tensor B^{μ} and a_i^* is the length of $\mathbf{a}_i^*$. Further, the components of the temperature tensor of an atom in the basic structure are denoted by $(\mathsf{B}_{\mathsf{b}}^{\mu})_{ij}$ while the components of the temperature tensor of the same atom in the average structure are denoted by $(\mathsf{B}_{\mathsf{a}}^{\mu})_{ij}$. For small amplitudes $C_{k_u}^{\mu}$ [(3.14)] and in a low-order approximation [see condition (3.30)], one can easily show, by use of (3.54) for the temperature factor and (3.20) for the atomic modulation factor, that the relation between these components can be written as

$$(\mathsf{B}_{\mathsf{a}}^{\mu})_{ij} = (\mathsf{B}_{\mathsf{b}}^{\mu})_{ij} + 4\pi^2\sum_{k_u=1}^{K_u}(\mathsf{U}_{k_u}^{\mu})_{ij}(a_i^*a_j^*)^{-1}, \tag{3.55}$$

where the $(\mathsf{U}_{k_u}^{\mu})_{ij}$, defined by (3.15), are the components of the K_u symmetric tensors $\mathsf{U}_{k_u}^{\mu}$. This clearly shows that the displacive modulation of an atom introduces an extra temperature factor. Note that, as long as the multiple summation in (3.20) can be approximated

by the term given by condition (3.30), equation (3.55) can also be used for structures where displacive modulation occurs together with density modulation.

As for nonmodulated crystals, the temperature tensors $\mathsf{B}^{\mu}_{\mathrm{b}}$ and $\mathsf{B}^{\mu}_{\mathrm{a}}$ can be reduced to the effective isotropic temperature parameters $B^{\mu}_{\mathrm{b,eff}}$ and $B^{\mu}_{\mathrm{a,eff}}$, respectively (Hamilton, 1959). Then, by use of (3.3), (3.4), (3.15) and (3.36), the relation between these parameters can be obtained from (3.55) as

$$B^{\mu}_{\mathrm{a,eff}} = B^{\mu}_{\mathrm{b,eff}} + \frac{4\pi^2}{3} \sum_{k_u=1}^{K_u} (U^{\mu}_{k_u})^2. \tag{3.56}$$

One can now write down a relation between the overall isotropic temperature parameters $B_{\mathrm{b,eff}}$ of the basic structure and $B_{\mathrm{a,eff}}$ of the average structure. If, as usual, overall temperature parameters are defined as weighted averages over atomic temperature parameters, then it follows from (3.56) that

$$B_{\mathrm{a,eff}} = B_{\mathrm{b,eff}} + \frac{4\pi^2}{3} U^2, \tag{3.57}$$

where the effect of the displacive modulation is accounted for by the overall modulation amplitude U defined by

$$U = \left(\sum_{k_u=1}^{K_u} U^2_{k_u} \right)^{1/2}, \tag{3.58}$$

with the amplitudes U_{k_u} given by (3.49).

References

BEVINGTON, P. R. (1969). *Data Reduction and Error Analysis for the Physical Sciences.* New York: McGraw-Hill.

GIACOVAZZO, C. (1980). *Direct Methods in Crystallography.* London: Academic.

GRADSHTEYN, I. S. & RYZHIK, M. (1980). *Table of Integrals, Series, and Products.* London: Academic.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HAO, Q., LIU, Y.-W. & FAN, H.-F. (1987). *Acta Cryst.* A**43**, 820–824.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

KOWALIK, J. & OSBORNE, M. R. (1968). *Methods for Unconstrained Optimization Problems.* New York: Elsevier.

LAM, E. J. W., BEURSKENS, P. T. & SMAALEN, S. VAN (1992*a*). *Solid State Commun.* **82**, 345–349.

LAM, E. J. W., BEURSKENS, P. T. & SMAALEN, S. VAN (1992*b*). *Z. Kristallogr. Supplement Issue No.* **6**, 349.

LAM, E. J. W., BEURSKENS, P. T. & SMAALEN, S. VAN (1993). *Acta Cryst.* A**49**, 709–721.

LAM, E. J. W., GELDER, R. DE, BEURSKENS, P. T., SMAALEN, S. VAN, FAN, H.-F. & LI, F.-H. (1994). To be published.

PÉREZ-MATO, J. M., MADARIAGA, G. & TELLO, M. J. (1986). *J. Phys. C: Solid State Phys.* **19**, 2613–2622.

PETŘÍČEK, V., COPPENS, P. & BECKER, P. (1985). *Acta Cryst.* A**41**, 478–483.

PETŘÍČEK, V. & COPPENS, P. (1988). *Acta Cryst.* A**44**, 235–239.

WILSON, A. J. C. (1942). *Nature (London)* **150**, 151–152.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258–261.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.

XIANG, S.-B., FAN, H.-F., WU, X.-J. & LI, F.-H. (1990). *Acta Cryst.* A**46**, 929–934.

YAMAMOTO, A. (1982). *Acta Cryst.* A**38**, 87–92.

YAMAMOTO, A. (1985). *REMOS85, computer program for the refinement of modulated structures.* National Institute for Research in Inorganic Materials, Sakura-Mura, Niihari-Gun, Ibaraki, 305, Japan.

4

Intensity Statistics and Normalized Structure Factors for Crystals with an Incommensurate One-Dimensional Modulation*

Dedicated to Professor A. J. C. Wilson on the occasion of the fiftieth anniversary of the 'Wilson Statistics'.

Abstract

An analytical expression is derived for the probability density function (p.d.f.) of X-ray structure-factor amplitudes of a crystal with an incommensurate one-dimensional modulation. The influence of the $(3+1)$-dimensional superspace symmetry is taken into account. It is shown that, in first-order approximation, this p.d.f. has the same functional form as the p.d.f. for a nonmodulated crystal, with a suitable modification of the atomic form factor. For main reflections and satellite reflections, an expression for the average intensity is derived. This leads to a definition of normalized structure factors for a crystal with an incommensurate one-dimensional modulation. In the same first-order approximation, the p.d.f. for the amplitudes of these normalized structure factors is identical to the p.d.f. for a nonmodulated crystal and does not distinguish between main reflections and satellite reflections. The theoretical p.d.f.s are compared to p.d.f.s obtained from X-ray diffraction data of some incommensurate one-dimensionally modulated crystals.

*Published as: Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1993). *Acta Crystallographyca*, A**49**, 709–721. Because modern journals require very condensed articles, a full derivation of the probability density functions has not been included in the article; it is presented here as Appendix *B*.

4.1 Introduction

An incommensurately modulated crystal can be described as a three-dimensional translationally symmetric structure (the basic structure), upon which a periodic deviation is superimposed. The wavelength of the deviation is incommensurate with respect to the lattice of the basic structure, thus destroying the three-dimensional lattice symmetry. The diffraction pattern of an incommensurately modulated crystal consists of main reflections at the nodes of the reciprocal lattice of the basic structure, accompanied by satellite reflections that are usually weaker. The intensity of a main reflection is mainly determined by the presence of averaged atoms at their average positions in the basic structure, while the intensity of a satellite reflection essentially depends on the degree of deviation from this basic structure.

During the last two decades there has been increasing interest in incommensurately modulated crystals. The structures of a few hundred of such compounds have been determined from single-crystal X-ray diffraction experiments. The standard procedure is to first determine the (nonmodulated) average structure by classical methods (direct methods and/or Patterson methods) and then to determine the modulation by trial and error by searching for anomalously large temperature factors in the average structure or from the higher-dimensional Patterson function (Steurer, 1987).

Direct methods have been applied to X-ray diffraction data in only one instance (Hao, Liu & Fan, 1987). A symbolic-addition procedure (Karle & Karle, 1966) and a modified Sayre-tangent formula were employed, with common structure factors substituted for normalized structure factors.

As a first step towards the application of statistical methods to modulated crystals, investigations have been carried out into X-ray diffraction intensity distributions as functions of $(\sin\theta)/\lambda$ and into the possibility of obtaining an overall modulation amplitude from the experimental data of crystals with an incommensurate one-dimensional displacive modulation (Lam, Beurskens & van Smaalen, 1992). In the present paper, the probability density function (p.d.f.) of the structure-factor amplitude is derived for crystals with an incommensurate one-dimensional displacive modulation and/or an occupancy-factor modulation. It is shown that this p.d.f. can be used to define normalized structure factors for modulated crystals.

4.2 The structure factor

Let the unit cell of the basic structure be spanned by vectors $\mathbf{a}_i$ $(i = 1, 2, 3)$ The reciprocal basic vectors $\mathbf{a}_i^*$ are defined by $\mathbf{a}_i^* \cdot \mathbf{a}_j = \delta_{ij}$ The position of an atom μ is given by $\mathbf{r}_{0,\mathbf{L}}^{\mu} = \mathbf{L} + \mathbf{r}_0^{\mu}$, where $\mathbf{L}$ is a basic-structure lattice-vector and $\mathbf{r}_0^{\mu}$ is the relative position of the atom in the unit cell Each atom is further characterized by its form factor f_0^{μ} and temperature tensor B_0^{μ}

The atomic modulation functions $\mathbf{u}^{\mu}(\mathbf{q}\ \ \mathbf{r}_{0,\mathbf{L}}^{\mu})$ and $p^{\mu}(\mathbf{q}\ \ \mathbf{r}_{0,\mathbf{L}}^{\mu})$ denote the deviations from the basic-structure position and occupancy factor, respectively They are periodic functions with period 1 The modulation wave vector $\mathbf{q}$ is incommensurate with respect to the reciprocal lattice of the basic structure The position and occupancy factor of an atom in the one-dimensionally modulated crystal are given by $\mathbf{r}_{\mathbf{L}}^{\mu} = \mathbf{r}_{0,\mathbf{L}}^{\mu} + \mathbf{u}^{\mu}(\mathbf{q}\ \ \mathbf{r}_{0,\mathbf{L}}^{\mu})$ and $p_{\mathbf{L}}^{\mu} = p^{\mu}(\mathbf{q} \cdot \mathbf{r}_{0,\mathbf{L}}^{\mu})$, respectively

The modulated crystal is embedded in $(3 + 1)$-dimensional superspace, giving a four-dimensional translationally symmetric supercrystal The argument $\mathbf{q}\ \ \mathbf{r}_{0\,\mathbf{L}}^{\mu}$ of the atomic modulation functions is replaced by $\bar{x}_4^{\mu} \equiv \mathbf{q}\ \ \mathbf{r}_{0,\mathbf{L}}^{\mu} + t$, where t is a continuous parameter along the extra dimension spanned by $\mathbf{e}_4$ This vector is perpendicular to physical space The position of an 'atom' in the supercrystal is given by the set of points $t \in \mathbb{R}$ at fixed $\mathbf{r}_{0,\mathbf{L}}^{\mu}$ having coordinates $(x_1^{\mu}, x_2^{\mu}, x_3^{\mu}, x_4^{\mu})$, where $x_i^{\mu} = [\mathbf{r}_{0,\mathbf{L}}^{\mu} + \mathbf{u}^{\mu}(\bar{x}_4^{\mu})]\ \ \mathbf{a}_i^*$ $(i = 1, 2, 3)$ and $x_4^{\mu} = \bar{x}_4^{\mu} + \mathbf{q} \cdot \mathbf{u}^{\mu}(x_4^{\mu})$, with respect to the basic translation vectors $\mathbf{b}_i = \mathbf{a}_i - (\mathbf{q}\ \ \mathbf{a}_i)\,\mathbf{e}_4$ $(i = 1, 2, 3)$ and $\mathbf{b}_4 = \mathbf{e}_4$ of the supercrystal Thus each 'atom' in the supercrystal is a 'string' along $\mathbf{e}_4$ with periodic bends and densifications caused by the atomic modulations Physical space is obtained as an intersection of superspace at constant t Different values for t lead to equivalent descriptions of physical space (de Wolff, 1974)

The symmetry of the supercrystal is described by a $(3 + 1)$-dimensional superspace group A symmetry operator is denoted by $(\mathsf{R}\,\varepsilon|v_1, v_2, v_3, v_4)$, where R is the three-dimensional part of the point-group operator, $\varepsilon = \pm 1$ and the numbers v_i are the components of a four-dimensional translation vector with respect to the basic vectors $\mathbf{b}_i$ of the supercrystal The operators $(\mathsf{R}|\mathbf{v})$, with $\mathbf{v} = \sum_{i=1}^{3} v_i\,\mathbf{a}_i$, are elements of the three-dimensional external space group of the superspace group It is assumed here that the external space group is identical to the basic structure space group, so that there is a one-to-one correspondence between symmetry-independent atoms' in the supercrystal and symmetry-independent atoms in the basic structure (de Wolff, Janssen & Janner, 1981, Janner, Janssen & de Wolff, 1983)

Because the modulation wave vector is incommensurate, there exists a one-to-one correspondence between reciprocal-lattice vectors in $(3 + 1)$-dimensional superspace and

reciprocal-lattice vectors in three-dimensional reciprocal space. Diffraction vectors in three-dimensional reciprocal space are defined as $\mathbf{S} = \mathbf{H} + m\,\mathbf{q}$, where $\mathbf{H}$ is a reciprocal-lattice vector of the basic structure and m is the integer satellite index. For a given incommensurate modulation wave vector, this decomposition is unique. There are two kinds of reflections: main reflections ($m = 0$) and satellite reflections ($m \neq 0$). The order of a reflection is given by $|m|$.

The structure factor for X-ray scattering (de Wolff, 1974; Yamamoto, 1982) can be rewritten as

$$F(\mathbf{S},m) = \epsilon(\mathbf{S}) \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon(\mathbf{S})} |g^\mu(\mathbf{S}\cdot\mathsf{R}_k, \varepsilon_k m)|\, f^\mu(\mathbf{S}\cdot\mathsf{R}_k) \times \exp\left[2\pi i(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + m v_4^k) + i\theta^\mu(\mathbf{S}\cdot\mathsf{R}_k, \varepsilon_k m)\right], \quad (4.1)$$

with the real atomic scattering factor for vibrating atoms defined by

$$f^\mu(\mathbf{S}) = f_0^\mu(|\mathbf{S}|)\exp(-\mathbf{S}\cdot\mathsf{B}_0^\mu\cdot\mathbf{S}) \quad (4.2)$$

and the atomic modulation factor $g^\mu(\mathbf{S},m) \equiv |g^\mu(\mathbf{S},m)|\exp[i\theta^\mu(\mathbf{S},m)]$ given by

$$g^\mu(\mathbf{S},m) = \int_0^1 p^\mu(\tau + \mathbf{q}\cdot\mathbf{r}_0^\mu)\exp\{2\pi i[\mathbf{S}\cdot\mathbf{u}^\mu(\tau+\mathbf{q}\cdot\mathbf{r}_0^\mu) + m\tau]\}\,\mathrm{d}\tau, \quad (4.3)$$

where the integration extends over one period along $\mathbf{e}_4$. Because the atomic scattering factor is a real function and because $g^\mu(-\mathbf{S},-m) = [g^\mu(\mathbf{S},m)]^*$, where * denotes the complex conjugate, Friedel's law applies to the structure factor.

Special attention is required for the appearance of the average atomic position $\mathbf{r}_0^\mu$ in (4.3), the expression for the atomic modulation factor $g^\mu(\mathbf{S},m)$. In agreement with common usage (de Wolff, 1974; Yamamoto, 1982), the atomic modulation functions $p^\mu(\bar{x}_4^\mu)$ and $\mathbf{u}^\mu(\bar{x}_4^\mu)$ are defined with respect to $\mathbf{r}_0^\mu$. Consequently, the definitions of these functions depend on $\mathbf{r}_0^\mu$. In contrast to common usage, the scalar product $\mathbf{q}\cdot\mathbf{r}_0^\mu$, which usually appears in the exponential part of the structure-factor expression, has been included in the expression for $g^\mu(\mathbf{S},m)$. If this had not been done, a variation of $\mathbf{r}_0^\mu$ would have caused a correlated change of the values of the atomic modulation functions (Figure 4.1*a*), causing the phase of $g^\mu(\mathbf{S},m)$ to vary with $\mathbf{r}_0^\mu$. However, by including $\mathbf{q}\cdot\mathbf{r}_0^\mu$ in $g^\mu(\mathbf{S},m)$, a variation of $\mathbf{r}_0^\mu$ also introduces a shift in the arguments of the atomic modulation functions, which cancels the effect of the changes in their definitions. As a result, the values of the atomic modulation functions are independent of $\mathbf{r}_0^\mu$ (Figure 4.1*b*). (See Appendix *A*.) It follows that $g^\mu(\mathbf{S},m)$ is an atomic property, independent of the average position $\mathbf{r}_0^\mu$ of the

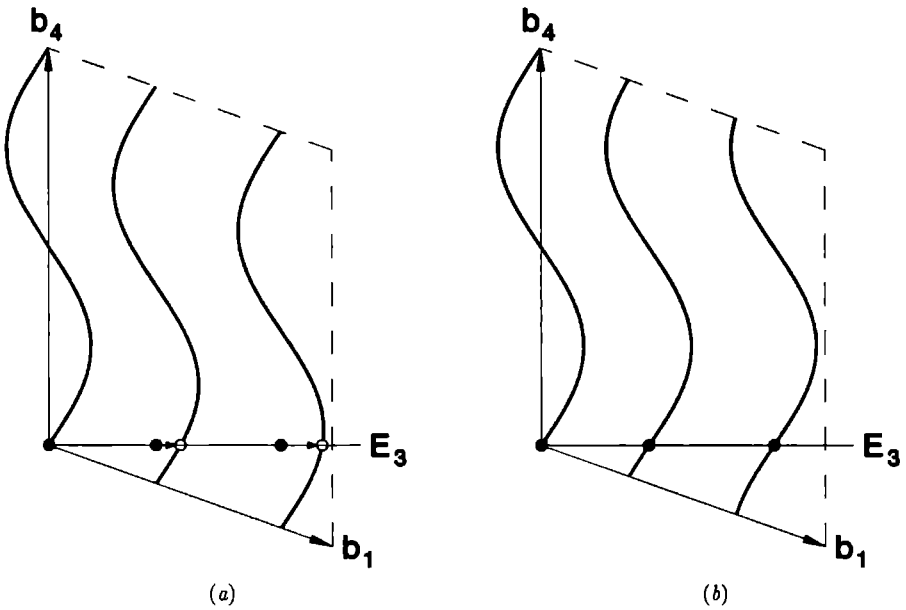


Figure 4.1. Dependency of the definition of the atomic modulation function on $\mathbf{r}_0^\mu$. Sections of superspace through $\mathbf{b}_1$ and $\mathbf{b}_4$ are shown. Physical space is denoted by the line E_3. A single superspace atom μ, having a displacive modulation only, is displayed at three different average positions $\mathbf{r}_0^\mu$ (denoted • in E_3). For each position, only one period of the atomic modulation function is shown. (*a*) In this example, the atomic modulation functions are defined by $\mathbf{u}^\mu(\bar{x}_4^\mu, \mathbf{r}_0^\mu) = \mathbf{U}^\mu \sin(2\pi\bar{x}_4^\mu)$, where $\bar{x}_4^\mu = \mathbf{q}\ \mathbf{r}_{0,\mathbf{L}}^\mu + t$ and $\mathbf{U}^\mu$ is a constant vector. Note that this choice is independent of the parameter $\mathbf{r}_0^\mu$. These functions are drawn for three different positions $\mathbf{r}_0^\mu$. The atomic displacements in E_3, denoted •→∘, vary with $\mathbf{r}_0^\mu$. (*b*) The atomic modulation functions are defined by $\mathbf{u}^\mu(\bar{x}_4^\mu, \mathbf{r}_0^\mu) = \mathbf{U}^\mu \sin[2\pi(x_4^\mu - \mathbf{q}\ \mathbf{r}_0^\mu)]$, where $\bar{x}_4^\mu$ and $\mathbf{U}^\mu$ are the same as in (*a*). The form of this function depends on $\mathbf{r}_0^\mu$, but the atomic displacements in E_3 are all the same (• = ∘).

atom. Consequently, the average atomic positions $\mathbf{r}_0^\mu$ can be used as independent random variables (see Section 4.3). Note that $g^\mu(\mathbf{S}, m)$ is a property not of one single atom in the basic-structure unit cell but of the collection of all atoms in the modulated crystal having average positions related to one another by basic-structure lattice translations.

The set of K symmetry operators obtained from the superspace group by factoring out all four-dimensional lattice translations generates K different symmetry-equivalent positions. This set includes the lattice-centering operations. The symmetry-enhancement factor $\epsilon(\mathbf{S})$ is defined, analogously to the case for nonmodulated crystals (Giacovazzo, 1980), as the number of times the condition $\mathbf{S}\ \mathsf{R}_k = \mathbf{S}$ is satisfied for all symmetry operators in

this set. For a nonsystematically absent reflection $\mathbf{S}$, it follows that, because of symmetry, each term in the structure-factor expression appears $\epsilon(\mathbf{S})$ times. Therefore, the second summation in (4.1) only counts those symmetry operators that generate $K/\epsilon(\mathbf{S})$ different diffraction vectors. The transformation rules for the atomic modulation functions were used to perform this symmetry-reduction procedure (Yamamoto, 1982).

The first summation in (4.1) counts the N/K symmetry-independent atoms in the modulated crystal, with N being the total number of atoms in the unit cell of the basic structure (none of which are on special positions).

For a phase-restricted reflection, there exists an operator $(\mathsf{R}_{k_0}\,\varepsilon_{k_0}|v_1^{k_0}, v_2^{k_0}, v_3^{k_0}, v_4^{k_0})$, in the second summation of (4.1), for which $\mathbf{S}\cdot\mathsf{R}_{k_0} = -\mathbf{S}$. This operator can be factored out of this summation so that the number of symmetry operators is further reduced by a factor of two and the structure factor becomes

$$F(\mathbf{S},m) = 2\epsilon(\mathbf{S})\exp[i\varphi_1(\mathbf{S})]\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/[2\epsilon(\mathbf{S})]}|g^\mu(\mathbf{S}\cdot\mathsf{R}_k,\varepsilon_k m)|\,f^\mu(\mathbf{S}\cdot\mathsf{R}_k)\times$$
$$\cos\left[2\pi(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + mv_4^k) + \theta^\mu(\mathbf{S}\cdot\mathsf{R}_k,\varepsilon_k m) - \varphi_1(\mathbf{S})\right], \quad (4.4)$$

where, because Friedel's law applies, $\varphi_1(\mathbf{S})$ is given by

$$\varphi_1(\mathbf{S}) = \pi(\mathbf{H}\cdot\mathbf{v}_{k_0} + mv_4^{k_0}). \quad (4.5)$$

The phase of the structure factor is now restricted to two values, $\varphi_1(\mathbf{S})$ and $\varphi_1(\mathbf{S}) + \pi$. Phase-restricted reflections have p.d.f.s different from those of non-phase-restricted reflections (Wilson, 1949).

The following abbreviations are used in this paper: $F \equiv F(\mathbf{S},m)$, $\epsilon \equiv \epsilon(\mathbf{S})$, $f_k^\mu \equiv f^\mu(\mathbf{S}\mathsf{R}_k)$, $g_k^\mu \equiv g^\mu(\mathbf{S}\mathsf{R}_k,\varepsilon_k m)$, $\theta_k^\mu \equiv \theta^\mu(\mathbf{S}\mathsf{R}_k,\varepsilon_k m)$ and $\varphi_1 \equiv \varphi_1(\mathbf{S})$. Trivial arguments are omitted in some of the functions defined below, to shorten the corresponding equations.

4.3 The probability density function

The probability density function (p.d.f.), $P_{|F|,\Phi}$, for the amplitude $|F|$ and phase Φ of the structure factor measures the chance, $P_{|F|,\Phi}(R,\varphi)\,\mathrm{d}R\,\mathrm{d}\varphi$, of finding $|F|$ with a numerical value between R and $R + \mathrm{d}R$ and Φ with a numerical value between φ and $\varphi + \mathrm{d}\varphi$. For crystals having three-dimensional lattice periodicity, the p.d.f. is obtained for a single diffraction vector by averaging over all configurations of symmetry-independent atoms in the unit cell, with the assumption that the positions of these atoms can be treated as

independent random variables. The same assumption is made with respect to the average positions $\mathbf{r}_0^\mu$ of the symmetry-independent atoms in the basic-structure unit cell of the modulated crystal, but with unchanging atomic modulations.

It is also assumed that the symmetry-independent atoms are uniformly distributed throughout the basic-structure unit cell. As a consequence, the p.d.f. $P_{\mathbf{r}}$ for finding a configuration of symmetry-independent atoms must be a constant equal to $V^{-N/K}$, where V is the volume of the basic-structure unit cell (Hauptman & Karle, 1952, 1953; Karle & Hauptman, 1953).

Non-phase-restricted reflections

The derivation of the p.d.f. for the structure-factor amplitude of non-phase-restricted reflections is performed analogously to a procedure given by Castleden (1987) for X-ray structure factors of nonmodulated crystals.† The structure factor F given by (4.1) is a function of the average atomic positions $\mathbf{r}_0^\mu$, which are assumed to be independent random variables. Because $F = A + iB$, the p.d.f. $P_{A,B}$ for (A, B) having the numerical values (a, b) is given by

$$P_{A,B}(a,b) = (2\pi)^{-2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[-i(au + bv)]\, Q(u,v)\, \mathrm{d}u\, \mathrm{d}v, \tag{4.6}$$

where $Q(u,v) \equiv \langle \exp[i(Au + Bv)] \rangle$ is, by definition, the characteristic function of $P_{A,B}$. Because A and B are functions of the independent random variables $\mathbf{r}_0^\mu$, the characteristic function can also be written as an expectation value with respect to the p.d.f. $P_{\mathbf{r}}$ for the configurations of symmetry-independent atoms in the basic-structure unit cell:

$$Q(u,v) = \int_V \cdots \int_V \exp[i(Au + Bv)] P_{\mathbf{r}}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K})\, \mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}, \tag{4.7}$$

where the integrals are over the volume of the basic-structure unit cell.

Because $F = |F| \exp(i\Phi)$, the p.d.f. $P_{|F|,\Phi}$ for $(|F|, \Phi)$ having the numerical values (R, φ) can be derived. By the introduction of polar coordinates $a = R\cos\varphi$, $b = R\sin\varphi$, $u = \rho\cos\xi$ and $v = \rho\sin\xi$, and using $P_{|F|,\Phi}(R,\varphi)\, \mathrm{d}R\, \mathrm{d}\varphi = P_{A,B}(a,b)\, \mathrm{d}a\, \mathrm{d}b$, it follows from (4.6) that the p.d.f. for the structure factor can be written as

$$\begin{aligned} P_{|F|,\Phi}(R,\varphi) \;&=\; (2\pi)^{-2} R \int_0^{\infty} \int_0^{2\pi} \exp[-iR\rho\cos(\xi - \varphi)] \times \\ &\qquad Q(\rho\cos\xi, \rho\sin\xi)\, \rho\, \mathrm{d}\rho\, \mathrm{d}\xi. \end{aligned} \tag{4.8}$$

†For phase-restricted reflections, the phase of the structure factor is not a continuous random variable, as for non-phase-restricted reflections, but is a discrete random variable. Therefore, the p.d.f. for phase-restricted reflections [(4.16)] contains only one Fourier integral and not two, as is the case for non-phase-restricted reflections [(4.6) and (4.8)]. This means that the p.d.f. presented by Castleden (1987) is not valid for phase-restricted reflections.

By the same procedure as given by Castleden (1987), the exponent in (4.7) can be evaluated as an N/ϵ-tuple product over integers $n_{\mu,k}$, of the form

$$\sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n_{\mu,k}}(\rho\epsilon|g_k^\mu|f_k^\mu) \right] \times$$

$$\exp\left\{ \imath \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n_{\mu,k} \left[2\pi \left(\mathbf{S} \cdot \mathsf{R}_k \cdot \mathbf{r}_0^\mu + \mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \xi + \pi/2 \right] \right\}, \quad (4.9)$$

with J_n the nth-order Bessel function of the first kind.

By substitution of (4.9) for the exponent in (4.7) and with the *a priori* assumption of uniformly distributed atoms, the characteristic function can be evaluated. When performing the integration with respect to the average atomic positions, one should be aware that, for main reflections, the components of $\mathbf{S}$ are all integers while, for satellite reflections, at least one of the components of $\mathbf{S}$ is not an integer. Then, the expression for the characteristic function becomes

$$Q(\rho\cos\xi, \rho\sin\xi) = \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty}$$

$$\left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha_{\mu,j}^c) \exp(\imath\pi\alpha_{\mu,j}^c) \right] \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n_{\mu,k}}(\rho\epsilon|g_k^\mu|f_k^\mu) \right] \times$$

$$\exp\left\{ \imath \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n_{\mu,k} \left[2\pi \left(\mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \xi + \pi/2 \right] \right\}, \quad (4.10)$$

where

$$h(z) = \begin{cases} 1 & (z = 0) \\ (\pi z)^{-1} \sin(\pi z) & (z \neq 0) \end{cases} \quad (4.11)$$

and

$$\alpha_{\mu,j}^c = \sum_{k=1}^{K/\epsilon} n_{\mu,k} \left(\sum_{i=1}^{3} S_i R_{ij}^k \right). \quad (4.12)$$

Here, S_i is the ith component of the diffraction vector with respect to the reciprocal-lattice vectors $\mathbf{a}_i^*$ of the basic structure and R_{ij}^k is the ijth component of the matrix R_k.

For each term in the multiple summation of (4.10), the $\alpha_{\mu,j}^c$ form a set of $3N/K$ numbers. A term will not contribute to the multiple summation if there is an $\alpha_{\mu,j}^c$ in the set with a nonzero integer value. Note that, for main reflections, a term only contributes

to the multiple summation if the condition $\alpha^c_{\mu,j} = 0$ is fulfilled for all μ and j. [This is in agreement with condition (2) given by Castleden (1987).] For satellite reflections, there is no such condition because at least one of the coordinates of the diffraction vector is not an integer. However, terms in the multiple summation with some of the $\alpha^c_{\mu,j}$ not integers and all others zero decrease rapidly in magnitude.

Following Castleden (1987), the p.d.f. $P_{|F|,\Phi}$ for the structure factor is evaluated. The characteristic function (4.10) is substituted in (4.8) and the integral with respect to ξ is calculated by means of an integral equation for Bessel functions. It is noticed that, for each term with given integers $n_{\mu,k}$ in the resulting formula for $P_{|F|,\Phi}$, there exists a corresponding term with all the integers reversed in sign, being its complex conjugate. Therefore, the imaginary parts of all terms cancel and $P_{|F|,\Phi}$ is a real function. The phase of the structure factor is now integrated out so that the p.d.f. $P_{|F|}$ for the structure-factor amplitude is obtained as

$$P_{|F|}(R) = R \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty} G^c(R) \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \right] \times \cos\left(\sum_{\mu=1}^{N/K} \left\{ \pi \sum_{j=1}^{3} \alpha^c_{\mu,j} + \sum_{k=1}^{K/\epsilon} n_{\mu,k} \left[2\pi \left(\mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu \right] \right\} \right), \quad (4.13)$$

where

$$G^c(R) = \int_0^\infty \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n_{\mu,k}}(\rho\epsilon |g_k^\mu| f_k^\mu) \right] J_0(\rho R)\, \rho \, \mathrm{d}\rho \quad (4.14)$$

is an integral containing multiple products of Bessel functions and the condition exists that

$$\sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n_{\mu,k} = 0, \quad (4.15)$$

resulting from the integration with respect to φ and further reducing the number of terms contributing to the multiple summation.

Phase-restricted reflections

The p.d.f. for the structure factor amplitude of a phase-restricted reflection is evaluated following a procedure indicated by Peschar (1987). From the actual structure factor F' of the phase-restricted reflection, given by (4.4), a new structure factor $F = F' \exp(-i\varphi_1)$ can be obtained. Because $|F| = |F'|$, the p.d.f. for the structure-factor amplitude is the same

for both structure factors. The new structure factor F is a real function dependent on the average atomic positions $\mathbf{r}_0^\mu$, which are assumed to be independent random variables. The p.d.f. P_F for F having the numerical value c is given by

$$P_F(c) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(-icw) Q(w)\, \mathrm{d}w, \tag{4.16}$$

where $Q(w) \equiv \langle \exp(iFw) \rangle$ is by definition the characteristic function of P_F. Because F can be positive as well as negative, the p.d.f. $P_{|F|}$ for $|F|$ having the numerical value R is obtained from (4.16) as

$$P_{|F|}(R) = \pi^{-1} \int_{-\infty}^{\infty} \cos(wR) Q(w)\, \mathrm{d}w. \tag{4.17}$$

The characteristic function can also be written as the expectation value with respect to the p.d.f. $P_{\mathbf{r}}$ of the configurations of symmetry-independent atoms in the basic-structure unit cell:

$$Q(w) = \int_V \cdots \int_V \exp(iFw) P_{\mathbf{r}}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K})\, \mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}, \tag{4.18}$$

where the integrals are over the volume of the basic-structure unit cell.

The characteristic function is evaluated, using a procedure similar to the one given above, as

$$\begin{aligned} Q(w) \;=\; & \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/(2\epsilon)}=-\infty}^{\infty} \\ & \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha_{\mu,j}^d) \exp(i\pi\alpha_{\mu,j}^d) \right] \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n_{\mu,k}}(2w\epsilon |g_k^\mu| f_k^\mu) \right] \times \\ & \exp\left\{ i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k} \left[2\pi \left(\mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \varphi_1 + \pi/2 \right] \right\}, \end{aligned} \tag{4.19}$$

with the function h defined by (4.11) and the numbers

$$\alpha_{\mu,j}^d = \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k} \left(\sum_{i=1}^{3} S_i R_{ij}^k \right) \tag{4.20}$$

having the same meaning as the numbers $\alpha_{\mu,j}^c$ given by (4.12).

In order to evaluate the p.d.f. of the structure-factor amplitude, the integral in (4.17) is split into two parts, *i.e.* $\int_{-\infty}^{\infty} \ldots \mathrm{d}w \to \int_0^{\infty} \ldots \mathrm{d}w + \int_{-\infty}^{0} \ldots \mathrm{d}w$. After substitution of (4.19) in both integrals, the second integral is transformed by replacing all numbers $n_{\mu,k}$

by $-n_{\mu,k}$, because the summations may be reversed, and changing w into $-w$. Thus, the second integral becomes the complex conjugate of the first integral. The p.d.f. $P_{|F|}$ for the structure-factor amplitude then becomes

$$P_{|F|}(R) = 2\pi^{-1} \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/(2\epsilon)}=-\infty}^{\infty} G^d(R) \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha_{\mu,j}^d) \right] \times$$

$$\cos\left(\sum_{\mu=1}^{N/K} \left\{ \pi \sum_{j=1}^{3} \alpha_{\mu,j}^d + \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k} \left[2\pi \left(\mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \varphi_1 + \pi/2 \right] \right\} \right), \quad (4.21)$$

where

$$G^d(R) = \int_0^\infty \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n_{\mu,k}}(2w\epsilon |g_k^\mu| f_k^\mu|) \right] \cos(wR)\, \mathrm{d}w \quad (4.22)$$

is an integral containing multiple products of Bessel functions.

4.4 Approximated probability density functions

Exact evaluation of the integrals (4.14) and (4.22) is only possible for a few simple cases. For the general case, analytical expressions can be derived, but cannot be simplified. It is possible, however, to obtain a first-order approximation for p.d.f.s (4.13) and (4.21) by only considering the term in the series expansion with $n_{\mu,k} = 0$ for all μ and k. Then, the multiple products in the integrals (4.14) and (4.22) contain zero-order Bessel functions (J_0). For large N, the integrands only give a significant contribution to the integrals if the argument of J_0 is small. Therefore, the approximation $J_0(z) \simeq \exp(-z^2/4)$ can be used.

In addition, let $\mathcal{S}_n$ be defined as

$$\mathcal{S}_n \equiv \sum_{\mu=1}^{N} |g^\mu f^\mu|^n, \quad (4.23)$$

where the summation extends over all atoms in the basic-structure unit cell. If the symmetry operators are factored out as in Section 4.2 and the transformation rules for atomic modulation functions (Yamamoto, 1982) are used, it can be shown that (4.23) is identical to

$$\mathcal{S}_n = \begin{cases} c \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} |g_k^\mu f_k^\mu|^n & \text{(non-phase-restricted reflections)} \\ 2\epsilon \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} |g_k^\mu f_k^\mu|^n & \text{(phase-restricted reflections).} \end{cases} \quad (4.24)$$

In first-order approximation, the p.d.f. $P_{|F|}$ for a non-phase-restricted reflection (4.13) is written as

$$P_{|F|}(R) = R\int_0^\infty \rho \exp\left(-\tfrac{1}{4}\rho^2\epsilon\mathcal{S}_2\right) J_0(\rho R)\,\mathrm{d}\rho, \tag{4.25}$$

with $\mathcal{S}_2$ defined by (4.23). This integral can be evaluated [equation (6.631-4) of Gradshteyn & Rydzhik (1980)] to obtain:

$$P_{|F|}(R) = \frac{2R}{\epsilon\mathcal{S}_2}\exp\left(-\frac{R^2}{\epsilon\mathcal{S}_2}\right). \tag{4.26}$$

The p.d.f. $P_{|F|}$ for a phase-restricted reflection (4.21) can be written in first-order approximation as

$$P_{|F|}(R) = 2\pi^{-1}\int_0^\infty \exp\left(-\tfrac{1}{2}w^2\epsilon\mathcal{S}_2\right)\cos(wR)\,\mathrm{d}w, \tag{4.27}$$

with $\mathcal{S}_2$ defined by (4.23). Evaluation of this integral [equation (3.869-4) of Gradshteyn & Rydzhik (1980)] gives:

$$P_{|F|}(R) = \left(\frac{2}{\pi\epsilon\mathcal{S}_2}\right)^{1/2}\exp\left(-\frac{R^2}{2\epsilon\mathcal{S}_2}\right). \tag{4.28}$$

Note that for both (4.26) and (4.28), the condition $\mathcal{S}_2 > 0$ must be fulfilled.

P.d.f.s (4.26) and (4.28) show a close resemblance to p.d.f.s for nonmodulated crystals (Wilson, 1949, 1950). In fact, they can be obtained from the latter by replacement of the atomic form factors f^μ with $|g^\mu|f^\mu$, where $|g^\mu|$ is the amplitude of the atomic modulation factor [(4.3)]. The effect of the superspace symmetry is taken into account by the symmetry-enhancement factor ϵ, which is defined similarly as for nonmodulated crystals.

In the limit of diminishing modulation ($\mathbf{u}^\mu \to 0$, $p^\mu \to 1$), p.d.f.s (4.26) and (4.28) reduce to those for nonmodulated crystals. For main reflections ($m = 0$), $|g^\mu| \to 1$, $\mathcal{S}_2 \to \sum_{\mu=1}^N (f^\mu)^2$ and $P_{|F|}(R)$ becomes identical to the p.d.f. for a nonmodulated crystal. For satellite reflections ($m \neq 0$), $|g^\mu| \to 0$, $\mathcal{S}_2 \to 0$ and $P_{|F|}(R) \to 0$ for $R \neq 0$, *i.e.* the satellite reflections disappear.

4.5 Normalized structure factors

For nonmodulated crystals, normalized structure factors are defined by $E \equiv F\langle|F|^2\rangle^{-1/2}$, where (in first-order approximation) $\langle|F|^2\rangle = \epsilon\sum_{\mu=1}^N (f^\mu)^2$, with $\langle\ \rangle$ denoting an average over all configurations of symmetry-independent atoms in the unit cell. The same definition can be used for modulated crystals but with $\langle|F|^2\rangle \equiv \int_0^\infty R^2 P_{|F|}(R)\,\mathrm{d}R = \epsilon\mathcal{S}_2$, where $P_{|F|}$

is given by either (4.26) or (4.28). Thus, the following expression is obtained for normalized structure factors of modulated crystals:

$$E = F\,(\epsilon\,\mathcal{S}_2)^{-1/2}\,. \tag{4.29}$$

From (4.29), the p.d.f.s $P_{|E|}$ for a normalized structure-factor amplitude $|E|$ of a modulated crystal having a numerical value X can be derived. Introducing the transformation $X = R(\epsilon\,\mathcal{S}_2)^{-1/2}$ and using $P_{|E|}(X)\,\mathrm{d}X = P_{|F|}(R)\,\mathrm{d}R$, one can write the p.d.f. $P_{|E|}$ for non-phase-restricted reflections as

$$P_{|E|}(X) = 2X\,\exp\left(-X^2\right), \tag{4.30}$$

while for phase-restricted reflections it becomes

$$P_{|E|}(X) = \left(\frac{2}{\pi}\right)^{1/2} \exp\left(\frac{-X^2}{2}\right). \tag{4.31}$$

Note that (4.30) and (4.31) are independent of specific properties of the modulated crystal, as for nonmodulated crystals. Also note that these p.d.f.s are independent of the diffraction vector **S**, in contrast to p.d.f.s derived in previous sections.

With the present definition of normalized structure factors [(4.29)], neither the acentric p.d.f. [(4.30)] nor the centric p.d.f. [(4.31)] distinguishes between main reflections and satellite reflections. These p.d.f.s are identical to p.d.f.s for normalized structure-factor amplitudes of nonmodulated crystals, also in first-order approximation (Giacovazzo, 1980). The difference between the approach for nonmodulated crystals and the present approach for modulated crystals is in the definition and evaluation of $\mathcal{S}_2$ [(4.23)]. It follows that, with the present definition of normalized structure factors [(4.29)], the structure-factor statistics of modulated crystals are the same for both main and satellite reflections and are, in addition, identical to the structure-factor statistics of nonmodulated crystals.

As with nonmodulated crystals, normalized structure factors (4.29) can be associated with structure factors due to point atoms in a modulated crystal. Consequently, averaging over reciprocal space instead of physical space provides an equivalent method of obtaining p.d.f.s and expectation values. In particular, for any large set of reflections (general, zone, row), $\langle |E|^2 \rangle = 1$, regardless of whether or not this set contains main reflections, satellite reflections or main and satellite reflections. This can be derived by a straightforward calculation from (4.30) and (4.31).

For nonmodulated crystals, treated in the same approximation, $\langle |F|^2 \rangle$ can be estimated from experimental X-ray intensities with no prior knowledge of the crystal structure other

than the unit-cell contents (Wilson, 1942). In the present case, exact evaluation of $\langle|F|^2\rangle$, and likewise of $\mathcal{S}_2$ [(4.23)], also requires knowledge of the complete atomic modulation functions. To obtain an *a priori* estimate of the normalized structure-factor amplitudes, further approximations are necessary.

For crystals with an incommensurate one-dimensional displacive modulation, $\langle|F|^2\rangle$ can be estimated if an overall modulation amplitude is introduced that simulates the effect of the atomic displacements. Experimental $|E|$-values estimated from measured X-ray intensities (I) on a relative scale (corrected for Lorentz and polarization effects and absorption) are then defined by [equations (18) and (19) of Lam, Beurskens & van Smaalen (1992)]

$$|E_b|^2 = I\left\{\epsilon G(s;|m|)\sum_{\mu=1}^{N}[f_0^\mu(s)]^2\right\}^{-1}, \tag{4.32}$$

where f_0^μ is the form factor for atoms at rest and $s = (\sin\theta)/\lambda$. The function $G(s;|m|)$,

$$G(s;|m|) = K^{-2}\exp(-2Bs^2)\int_0^1 J_{|m|}^2(4\pi sUx)\,\mathrm{d}x, \tag{4.33}$$

only depends on the scale factor K, the overall isotropic temperature parameter B and the overall modulation amplitude U. These parameters can be obtained by fitting[‡] this function against (seminormalized) average intensities *versus* s^2.

4.6 Numerical evaluation

The validity of the approximate expressions (4.30) and (4.31) has been tested by calculating $|E_b|$ and $P_{|E_b|}$ from X-ray structure-factor data for several structures with an incommensurate one-dimensional displacive modulation. As for nonmodulated crystals, the assumptions underlying the approximations require a structure with many symmetry-independent equal atoms that are randomly distributed throughout the basic-structure unit cell. Here, also, a random distribution of the components of the atomic modulation functions is required. A first test for the theory was provided by fictitious structures devised as to fulfil these requirements as closely as possible. In addition, the effect of special atomic modulations on the p.d.f.s is examined. In the last part of this section, p.d.f.s for some real modulated crystals are shown.

Normalized structure-factor amplitudes $|E_b|$ were estimated from (4.32) using the previously defined fitting procedure to determine K, B and U (Lam, Beurskens & van Smaalen,

[‡]The fitting procedure (Lam, Beurskens & van Smaalen, 1992) was modified to perform a logarithmic fit. This automatically assigns a larger weight to weak intensity data and generally results in a better fit.

1992). The p.d.f. $P_{|E_b|}$ for the normalized structure-factor amplitudes was then calculated by counting the number of reflections within suitable $|E_b|$ intervals, and then multiplying this number by an appropriate normalization constant.

All the model structures created have superspace group $\mathrm{P1}(q_1, q_2, q_3)1$ (models $A1$–$A4$) or superspace group $\mathrm{P\bar{1}}(q_1, q_2, q_3)\bar{1}$ (models $C1$–$C4$). Each model structure has a realistic density (~ 18 Å^3 atom^{-1}) and realistic atomic modulations. The basic-structure unit cell contains 50 carbon atoms, with the symmetry-independent atoms randomly positioned and not occupying any special positions. For each symmetry-independent atom, the modulation function is given by $\mathbf{u}^\mu(\bar{x}_4^\mu) = \mathbf{U}_s^\mu \cos(2\pi\bar{x}_4^\mu) + \mathbf{U}_c^\mu \sin(2\pi\bar{x}_4^\mu)$, where the directions of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$ were chosen at random. The atomic modulation amplitude U_μ, defined by $U_\mu^2 = (U_s^\mu)^2 + (U_c^\mu)^2$ with U_s^μ and U_c^μ representing the lengths of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$, respectively, fluctuates around the overall modulation amplitude U. The latter is given by $U^2 = \sigma^{-1}\sum_{\mu=1}^N Z_\mu^2 U_\mu^2$, where $\sigma = \sum_{\mu=1}^N Z_\mu^2$ and Z_μ is the atomic number. To examine the effect of nonrandom atomic modulations, additional model structures were devised, having the same characteristics as those mentioned above but with a different type of atomic modulation. For one type of atomic modulation, the directions of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$ were chosen arbitrarily for each symmetry-independent atom but all atoms have identical modulation amplitudes. Another type of atomic modulation is the rigid-body displacement. For each symmetry-independent atom, the modulation function is given by $\mathbf{u}^\mu(\bar{x}_4^\mu) = (U_\mu/a_2)\sin(2\pi t)\,\mathbf{a}_2$, where $t = \bar{x}_4^\mu - \mathbf{q}\cdot\mathbf{r}_{0,\mathbf{L}}^\mu$, *i.e.* the modulation is a sinusoidal translation along the $\mathbf{a}_2$ axis of the basic-structure unit cell, with all atoms having the same starting phase and modulation amplitudes. Characteristics of the model structures together with details of all atomic modulations are given in Table 4.1. For all model structures, structure factors were calculated for main reflections and first-order satellites, up to $s = 1$ Å^{-1}, using $K = 1$ and $B = 2$ Å^2.

The values of the parameters K, B and U obtained from the fitting procedure are given in Table 4.2. For both small and medium-size atomic modulations, they are in excellent agreement with the values input to the structure-factor calculations. The largest deviations occur for the U values of structures $A3$ and $C3$. Also shown in Table 4.2 are the values of $\langle|E_b|^2\rangle$ calculated from the normalized structure-factor amplitudes $|E_b|$. For both main reflections and first-order satellites, these values are all close to 1, as they should be with the present definition of normalized structure factors [(4.29)]. Note that nonrandom atomic modulations do not apparently cause serious deviations from the ideal values. Figures 4.2(a) and (b) show the results of the fitting procedure for the noncentrosymmetric structure $A2$ and the centrosymmetric structure $C2$, respectively. One can see that the intensity distributions are accurately reproduced. For the structures $A3$ and $C3$, the quality

Table 4.1. Model structure characteristics

Compounds A_i, noncentrosymmetric superspace group $P1(q_1, q_2, q_3)1$, C_i, centrosymmetric superspace group $P\bar{1}(q_1, q_2, q_3)\bar{1}$ (see text for explanation)

Model structure	U (Å)	U_μ (Å) min /max	Atomic modulation functions
$A1$	0 04	0 012/0 055	Random amplitudes and directions
$A2$	0 2	0 057/0 276	Random amplitudes and directions
$A3$	0 2	0 2/0 2	Identical amplitudes and random directions
$A4$	0 2	0 2/0 2	Rigid body displacement
$C1$	0 04	0 019/0 051	Random amplitudes and directions
$C2$	0 2	0 097/0 255	Random amplitudes and directions
$C3$	0 2	0 2/0 2	Identical amplitudes and random directions
$C4$	0 2	0 2/0 2	Rigid body displacements

Table 4.2 Values of K, B, U and $\langle|E_b|^2\rangle$ for the model structures

Parameters K, B and U were obtained from a fitting procedure applied to main reflections and $|m| = 1$ satellites Values of $\langle|E_b{}^2\rangle$ were calculated from the normalized structure-factor amplitudes $|E_b|$ [equation (4 32)] for (I) main reflections, (II) $|m| = 1$ satellites and (III) main reflections plus $|m| = 1$ satellites These values must be compared to the input values $K = 1$, $B = 2$ and U as given in Table 4 1, while $\langle|E_b|^2\rangle = 1$

Model structure	K	B (Å^2)	U (Å)	$\langle\|E_b\|^2\rangle$ (I)	(II)	(III)
$A1$	1 00	1 99	0 040	0 991	1 003	0 994
$A2$	1 01	1 98	0 198	0 985	1 005	0 993
$A3$	1 04	1 91	0 214	0 973	1 011	0 994
$A4$	1 01	1 98	0 200	0 986	1 004	0 993
$C1$	0 99	2 00	0 040	0 994	1 002	0 995
$C2$	1 01	1 98	0 203	0 987	1 004	0 994
$C3$	1 02	1 94	0 212	0 987	1 008	0 994
$C4$	1 01	1 97	0 199	0 989	1 012	1 000

of the fitted intensity distributions for the main reflections (not shown here) is somewhat less The intensity distributions given in Figures 4 2(a) and (b) correspond well with the intensity distributions of all other noncentrosymmetric and centrosymmetric model structures, respectively

P d f s $P_{|E_b|}$ for structures $A2$ and $C2$ are given in Figure 4 3 The p d f s for main reflections and first-order satellites are nearly identical for each structure Furthermore, the p d f s for structures $A2$ and $C2$ are in excellent agreement with the theoretical p d f s for noncentrosymmetric [(4 30)] and centrosymmetric [(4 31)] structures respectively A

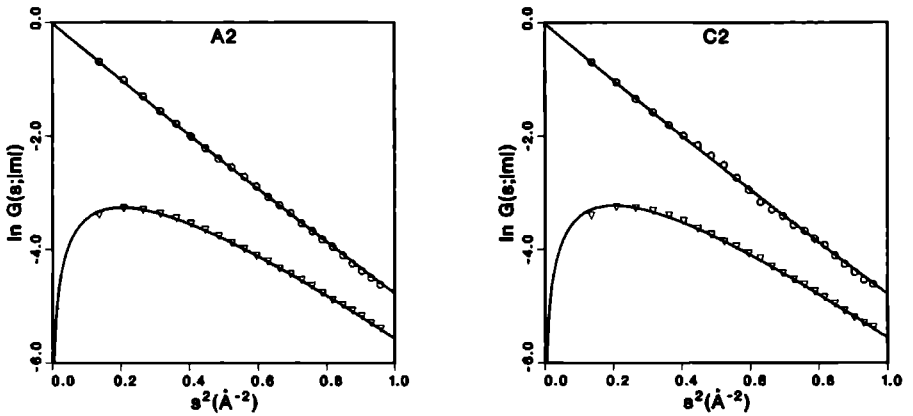


Figure 4.2. Natural logarithm of the (seminormalized) average intensity $G(s;|m|)$ as a function of s^2, for main reflections (circles) and $|m| = 1$ satellite reflections (triangles). The solid lines represent the curves obtained from the fitting procedure: (*a*) for structure $A2$; (*b*) for structure $C2$.

similar good agreement was observed for the p.d.f.s of the structures $A1$, $A3$, $C1$ and $C3$ (not shown here). This shows that, with the present definition of normalized structure factors [(4.29)], the structure-factor statistics do not distinguish between main and satellite reflections and are identical to the structure-factor statistics for nonmodulated crystals.

For the structures $A4$ and $C4$ (rigid-body modulations), the resulting p.d.f.s $P_{|E_b|}$ show entirely different behavior. For the noncentrosymmetric structure $A4$, the p.d.f. for main reflections is in between acentric and centric (Figure 4.4*a*), while the p.d.f. for first-order satellites follows the theoretical p.d.f. for centrosymmetric structures (Figure 4.4*b*). For the centrosymmetric structure $C4$, the p.d.f.s show severe deviations from the theoretical p.d.f., especially for low and intermediate $|E_b|$ values, indicating an excess of weak reflections. In fact, the p.d.f.s $P_{|E_b|}$ shown in Figures 4.4(*c*) and (*d*), show remarkable resemblance to hypercentric distributions as known for nonmodulated crystals (Shmueli, Weiss & Kiefer, 1985). Note that, for structures $A4$ and $C4$, the p.d.f.s tend to be more centric than expected. This effect is larger for first-order satellites than for main reflections, presumably because the intensities of satellite reflections are much more sensitive to the modulation than the intensities of main reflections.

In summary, restriction of the atomic displacements to having the same modulation amplitude for all atoms does not have much influence on the p.d.f.s. Also, restriction of the directions of the atomic displacement vectors introduces pseudosymmetry, causing the p.d.f.s to become more centric than they are expected to be. This effect is more severe for

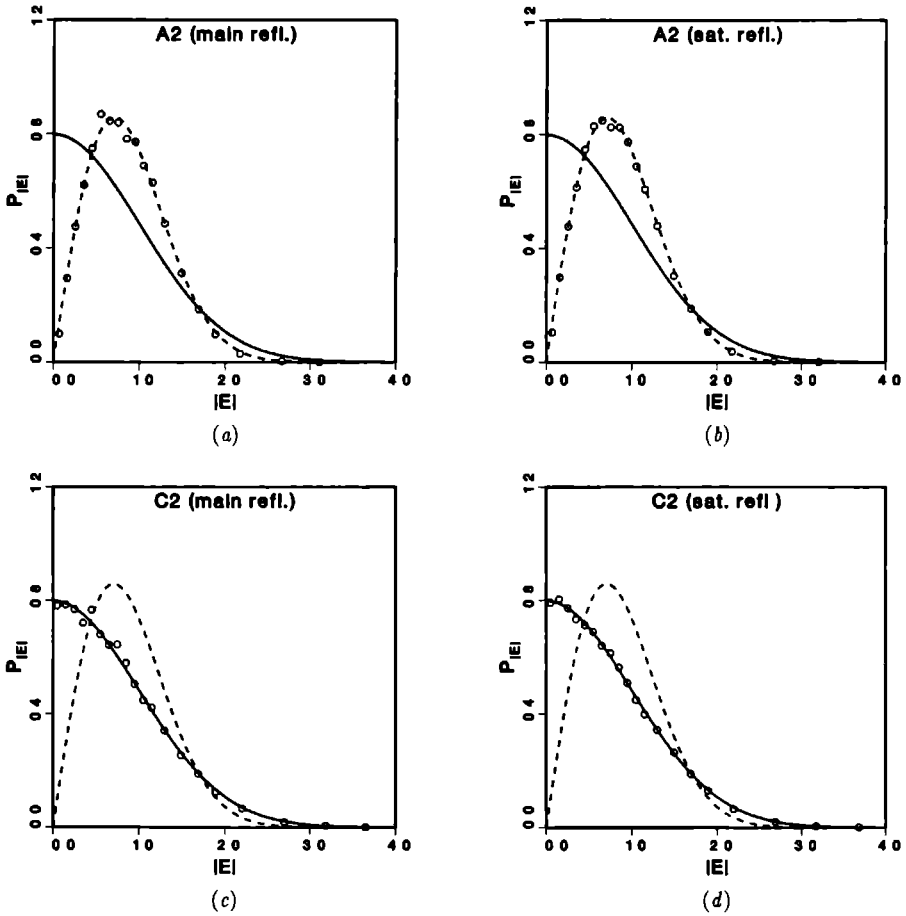


Figure 4.3. P d f s for model structures with random atomic modulations The solid line represents the theoretical p d f for normalized structure factor amplitudes of centrosymmetric structures [(4 31)] The dashed line represents the p d f for normalized structure factor amplitudes of noncentrosymmetric structures [(4 30)] Circles represent the p d f $P_{|E_b|}$ derived from the $|E_b|$ values [(4 32)] calculated for the various structures (*a*) for main reflections of structure *A*2 (*b*) for $|m| = 1$ satellites of structure *A*2, (*c*) for main reflections of structure *C*2 (*d*) for $|m| = 1$ satellites of structure *C*2

satellites than for main reflections An acentric p d f can even be changed into a centric p d f Although a rigorous mathematical treatment is not yet available, it seems that a special type of displacive modulation can introduce effects similar to hypersymmetry effects for nonmodulated crystals

For three real compounds with displacively modulated structures, intensity distributions and p d f s were calculated For Na_2CO_3 (van Aalst, den Hollander, Peterse & de

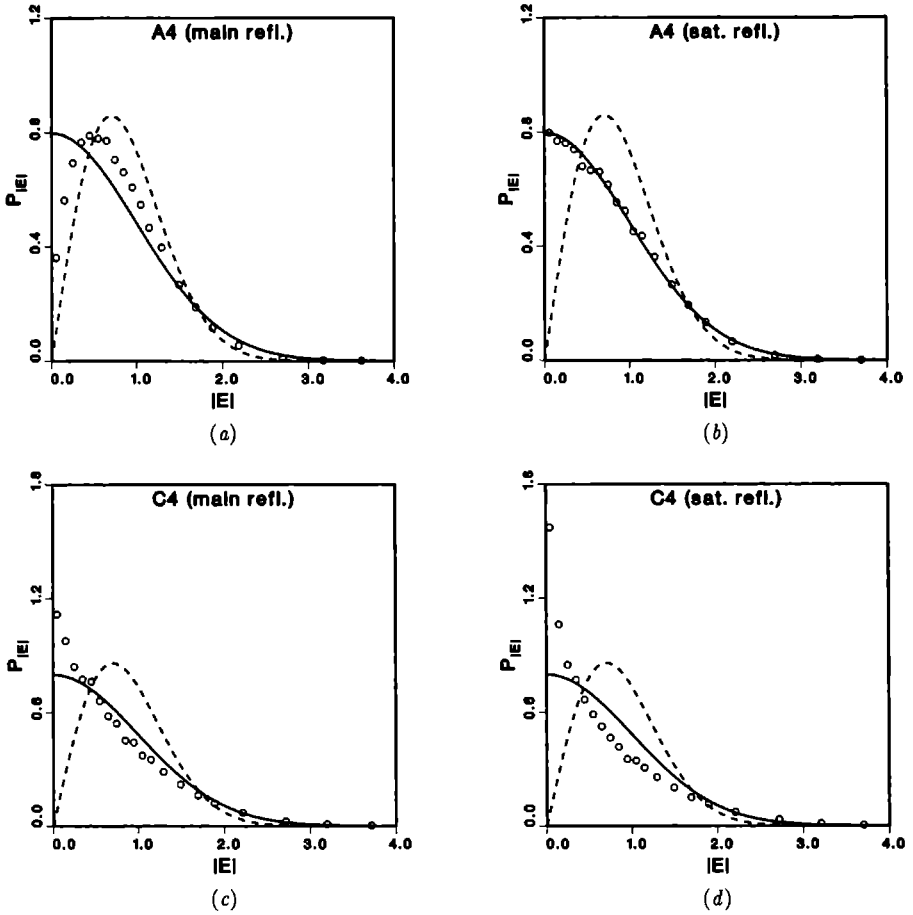


Figure 4.4. P d f s for structures with rigid-body modulations (see Figure 4 3 for definitions): (*a*) for main reflections of structure *A*4, (*b*) for $|m| = 1$ satellites of structure *A*4, (*c*) for main reflections of structure *C*4, (*d*) for $|m| = 1$ satellites of structure *C*4.

Wolff, 1976) and for $K_{0.3}MoO_3$ (Schutte, 1990), both the set of $|F|$ values derived from experiment and the more complete set of $|F|$ values derived from the published structure models were used. For $C_{12}D_{10}$ (deuterated biphenyl; Baudour & Sanquer, 1983), only the calculated $|F|$ values were available, as the structure was determined by neutron diffraction. For each compound, the published structural model was used to calculate the overall modulation amplitude U and, similarly, the overall isotropic temperature parameter B (Hamilton, 1959). For both main reflections and first-order satellites, structure factors were calculated with scale factor $K = 1$ and up to $s = 1$ Å^{-1}. Results obtained from

Table 4.3. Values of K, B, U and $\langle|E_b|^2\rangle$ for the real modulated compounds

Parameters K, B and U were obtained from a fitting procedure applied to main reflections and $|m| = 1$ satellites Values of $\langle|E_b|^2\rangle$ were calculated from the normalized structure-factor amplitudes $|E_b|$ [equation (4 32)] for (I) main reflections, (II) $|m| = 1$ satellites and (III) main reflections plus $|m| = 1$ satellites For each compound, line *pp* contains B and U calculated from published parameters and the expected values of $\langle|E_b|^2\rangle$, for calculated data, $K = 1$ For experimental data, K is unknown Lines f_c and f_o show the results obtained from calculated data and experimental X-ray data, respectively The values of K for experimental data cannot be compared to those for calculated data

Model structure		K	B (Å^2)	U (Å)	$\langle\|E_b\|^2\rangle$ (I)	(II)	(III)
Na_2CO_3	*pp*	1	1 42	0 386	1	1	1
	f_c	1 07	1 10	0 422	1 007	1 007	1 007
	f_o	0 60	1 16	0 461	0 997	1 009	1 005
$K_{0\,3}MoO_3$	*pp*	1	0 22	0 033	1	1	1
	f_c	1 04	0 15	0 035	0 995	1 001	0 999
	f_o	3 18	0 17	0 035	0 993	0 994	0 993
$C_{12}D_{10}$	*pp*	1	0 99	0 112	1	1	1
	f_c	1 05	0 70	0 110	0 998	1 008	1 005

the fitting procedure together with the values of $\langle|E_b|^2\rangle$ are summarized in Table 4 3 Apparently, all scale factors for the calculated structure factors are overestimated The scale factors for the observed X-ray intensities were not reported in the literature and cannot be compared to the scale factors input to the structure-factor calculations The fitted values for B and U are in reasonable agreement with *a priori* calculated values Note that the values of B and U obtained from the fitting procedure applied to calculated structure factors compare very well with those obtained from observed X-ray intensities, which shows that the deviations between calculated and fitted parameters are intrinsic to the structures and not a result of experimental errors The values of $\langle|E_b|^2\rangle$ are close to 1 for calculated structure factors as well as observed X-ray intensities

From Figure 4 5, it can be seen that the experimental intensity distributions are reasonably well reproduced for all three modulated crystals The p d f s for Na_2CO_3 (Figures 4 6*a* and *b*) and $K_{0\,3}MoO_3$ (Figures 4 6*c* and *d*) obtained from calculated structure-factor amplitudes are essentially centric, as expected from their superspace groups, but show hypercentric behavior This is likely to be caused by atoms on special positions, the nonrandom arrangement of atoms in the basic-structure unit cells and the nonrandom character of the atomic modulation, for Na_2CO_3 the atomic displacements are parallel to the $\mathbf{a}_2$ axis for most of the atoms The same deviations were also observed for p d f s of main reflec-

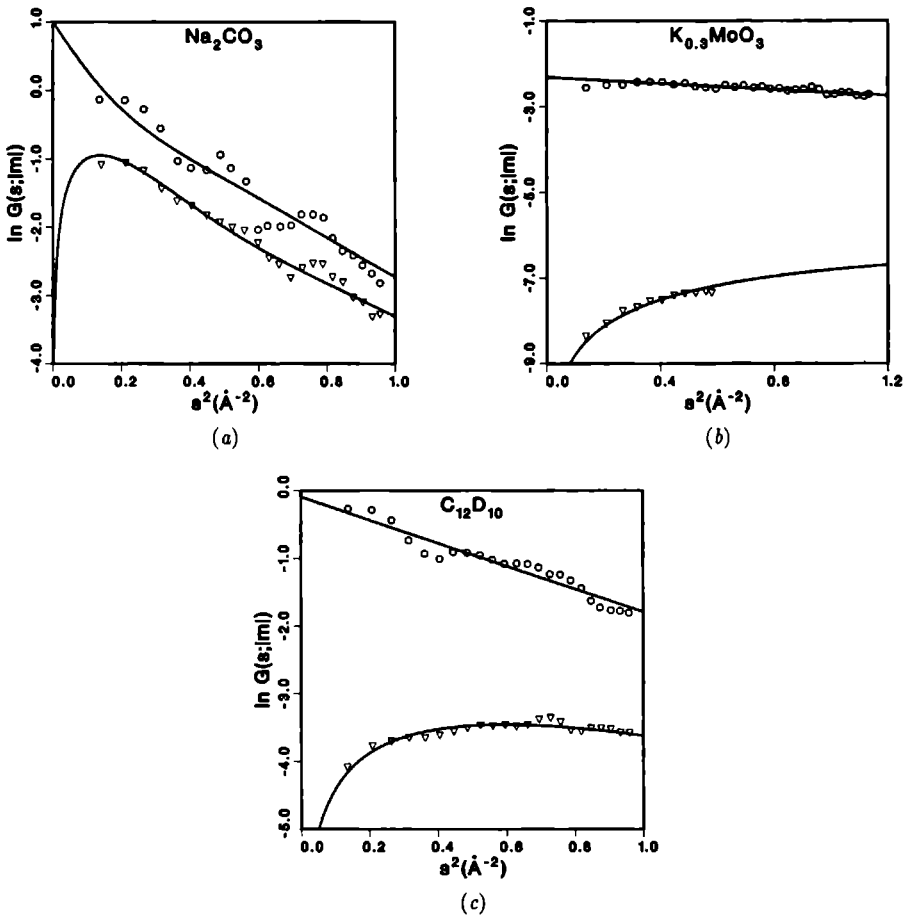
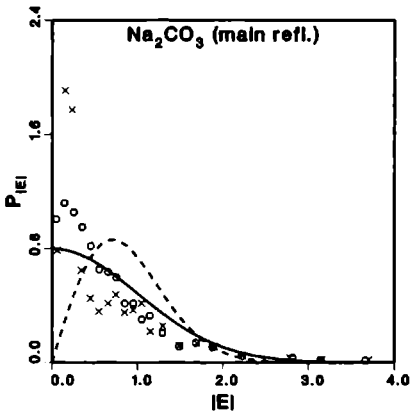


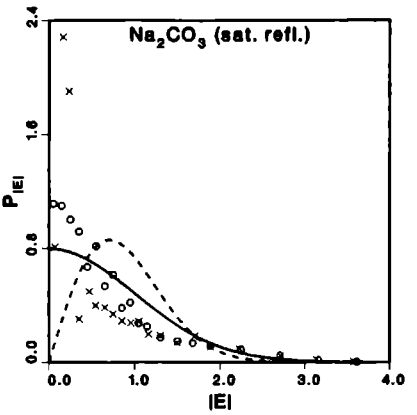
Figure 4.5. Natural logarithm of the (seminormalized) average intensity $G(s;|m|)$ as a function of s^2 (see Figure 4.2 for definitions): (*a*) Na_2CO_3; (*b*) $K_{0.3}MoO_3$; (*c*) deuterated biphenyl.

tions, using $|E|$ values obtained through a conventional Wilson plot (Wilson, 1942). This indicates that these anomalies are intrinsic to the structure. The behavior of the p.d.f.s obtained from calculated structure factors is smoother than that of those obtained from the experimental X-ray data. This is a result of the large number of reflections with intensities less than or equal to a few standard deviations. Note that the p.d.f.s have the same shape for main reflections and first-order satellites.

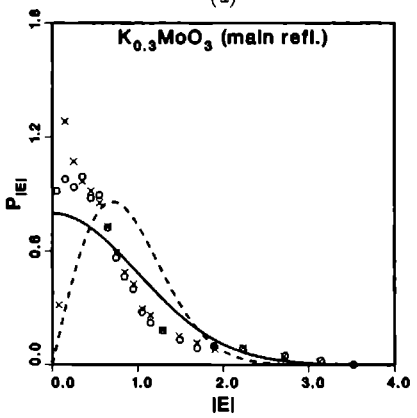
The p.d.f.s for $C_{12}D_{10}$ obtained from calculated structure factors show behavior that is more centric than acentric (Figures 4.6*e* and *f*), although the superspace group is non-


Na_2CO_3 (main refl.)
$P_{|E|}$
|E|
0.0
0.8
1.6
2.4
0.0
1.0
2.0
3.0
4.0

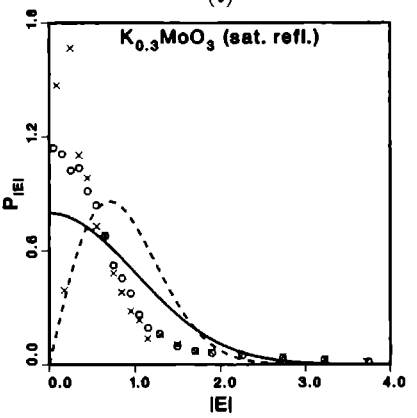
(a)


Na_2CO_3 (sat. refl.)
$P_{|E|}$
|E|
0.0
0.8
1.6
2.4
0.0
1.0
2.0
3.0
4.0

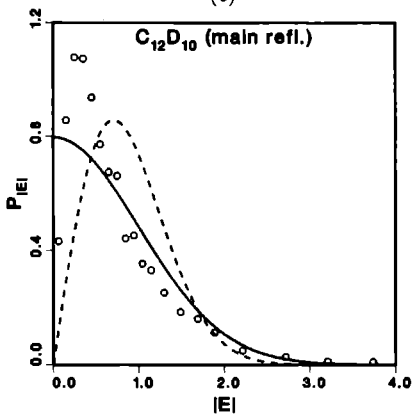
(b)


$K_{0.3}MoO_3$ (main refl.)
$P_{|E|}$
|E|
0.0
0.6
1.2
1.6
0.0
1.0
2.0
3.0
4.0

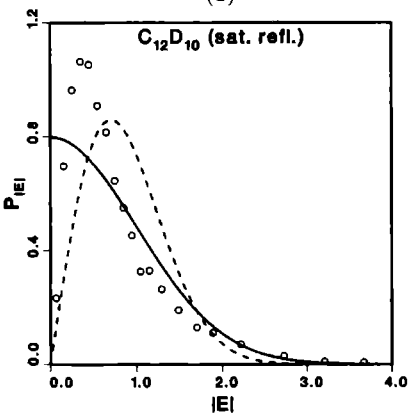
(c)


$K_{0.3}MoO_3$ (sat. refl.)
$P_{|E|}$
|E|
0.0
0.6
1.2
1.6
0.0
1.0
2.0
3.0
4.0

(d)


$C_{12}D_{10}$ (main refl.)
$P_{|E|}$
|E|
0.0
0.4
0.8
1.2
0.0
1.0
2.0
3.0
4.0

(e)


$C_{12}D_{10}$ (sat. refl.)
$P_{|E|}$
|E|
0.0
0.4
0.8
1.2
0.0
1.0
2.0
3.0
4.0

(f)

◁

Figure 4.6. P.d.f.s for several real structures with a displacive modulation (see Figure 4.3 for definitions); circles are obtained from calculated structure factors and crosses are obtained from experimental X-ray data: (*a*) for main reflections of Na_2CO_3; (*b*) for $|m| = 1$ satellites of Na_2CO_3; (*c*) for main reflections of $K_{0.3}MoO_3$; (*d*) for $|m| = 1$ satellites of $K_{0.3}MoO_3$; (*e*) for main reflections of $C_{12}D_{10}$; (*f*) for $|m| = 1$ satellites of $C_{12}D_{10}$.

centrosymmetric. This is a typical example of a modulated crystal with pseudosymmetry. In the basic structure (space group $P2_1/a$), there is an inversion centre at the centre of the molecule. This inversion centre is destroyed by the displacive modulation (specifically, by the torsion around the long molecular axis). This means that the superspace group is noncentrosymmetric (external space group Pa), but half of the symmetry-independent atoms have average positions $\mathbf{r}_0^\mu$ related to those of the other symmetry-independent atoms by an inversion centre. This causes the p.d.f.s to deviate from the theoretical p.d.f. [(4.30)].

4.7 Concluding remarks

A definition has been presented for normalized structure factors in X-ray diffraction for main reflections and satellite reflections of incommensurate one-dimensionally modulated crystals. For displacively modulated crystals, the normalized structure-factor amplitudes can be estimated from experimental X-ray intensity data using the previously defined fit of (seminormalized) average intensity *versus* $(\sin^2\theta)/\lambda^2$ (Lam, Beurskens & van Smaalen, 1992).

For both phase-restricted and non-phase-restricted reflections, theoretical expressions have been derived for centric and acentric p.d.f.s, respectively, of normalized structure-factor amplitudes. These p.d.f.s make no distinction between main reflections and satellite reflections and, in addition, are identical to p.d.f.s for normalized structure-factor amplitudes of nonmodulated crystals.

The theoretical p.d.f.s are in excellent agreement with p.d.f.s obtained from normalized structure-factor amplitudes of idealized model structures having many equal atoms randomly distributed throughout the basic-structure unit cell, none of them occupying special positions, with random atomic displacements. Model structures with special displacive modulations cause the p.d.f.s derived from X-ray intensities to deviate severely from the theoretical p.d.f.s. This is especially true for rigid-body displacements, which cause the experimental p.d.f.s to be more centric than the theoretical p.d.f.s and which can even change an acentric p.d.f. into a centric one.

For real modulated crystals, there is reasonable agreement between practical p.d.f.s and theoretical p.d.f.s, although various effects that also exist for nonmodulated crystals (Srinivasan & Parthasarathy, 1976) cause deviation from the theoretical p.d.f.s; for example, nonrandom atomic distribution and atoms on special positions. Deviations are also caused by special atomic modulations and by the destruction of symmetry elements by modulation, leading to pseudosymmetry.

The results obtained from the idealized model structures show the present definition of normalized structure factors to provide correct structure-factor statistics for incommensurately modulated crystals. Additional tests are in progress, investigating the reliability of the triplet phase relation and the tangent formula, using only large normalized structure-factor amplitudes. It is expected that, eventually, statistics of this kind will be used by direct-method procedures applied to incommensurately modulated crystals.

Acknowledgements

The authors thank A. Janner (University of Nijmegen) for many stimulating discussions and F. Tuinstra (Delft University of Technology) for supplying the experimental data on Na_2CO_3. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO).

Appendix A

The contribution of atom μ, having electron density ρ_μ, in basic-structure unit cell $\mathbf{L}$, to the electron density of the modulated crystal is

$$p^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)]\rho_\mu\{|\mathbf{r}-\mathbf{r}^\mu_{0,\mathbf{L}}-\mathbf{u}^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)]|\}. \tag{4.34}$$

The atomic modulation functions depend on the choice of the phase-reference point $\mathbf{g}^\mu$. This can be chosen arbitrarily for each atom (Petříček, Coppens & Becker, 1985). Therefore, the contribution (4.34) can also be written as

$$p'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)]\rho_\mu\{|\mathbf{r}-\mathbf{r}^\mu_{0,\mathbf{L}}-\mathbf{u}'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)]|\}, \tag{4.35}$$

with the atomic modulations described by functions p'^μ and $\mathbf{u}'^\mu$, defined with respect to another phase-reference point $\mathbf{g}'^\mu$.

Because (4.34) and (4.35) must describe the same electron density, they must be equal, which leads to

$$p^{\mu}[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^{\mu})] = p'^{\mu}[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^{\mu})], \tag{4.36}$$

$$\mathbf{u}^{\mu}[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^{\mu})] = \mathbf{u}'^{\mu}[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^{\mu})]. \tag{4.37}$$

Because the phase-reference points $\mathbf{g}^{\mu}$ and $\mathbf{g}'^{\mu}$ are independent of one another, the left- and right-hand sides of (4.36) and, similarly, of (4.37) must be independent of these phase-reference-points. Therefore, although the atomic modulation functions p^{μ} and $\mathbf{u}^{\mu}$, as well as their argument $\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^{\mu})$, depend on the choice of the phase-reference-point $\mathbf{g}^{\mu}$, the values of the atomic modulations are independent of this choice.

Appendix B

Non-phase-restricted reflections

Here, the derivation is presented of the probability density function (p.d.f.) for the structure-factor amplitude of non-phase-restricted reflections [(4.13)], starting by noticing that expression (4.1) for the structure factor, written as $F = A + iB$, is a complex function of the independent continuous random variables $\mathbf{r}_0^{\mu}$. It follows that the real and imaginary parts of the structure factor can be considered as independent continuous random variables themselves so that, in general, the p.d.f. for (A, B) having the numerical values (a, b) can be written as a two-dimensional Fourier transform [(4.6)]:

$$P_{A,B}(a,b) = (2\pi)^{-2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp[-i(au+bv)]\,Q(u,v)\,\mathrm{d}u\,\mathrm{d}v. \tag{4.38}$$

The characteristic function Q is by definition the inverse Fourier transform of $P_{A,B}$. Consequently, the characteristic function can be written as an expectation value with respect to the p.d.f. $P_{A,B}$:

$$Q(u,v) = \langle\exp[i(Au+Bv)]\rangle\,. \tag{4.39}$$

Because $P_{A,B}$ is unknown, the characteristic function (4.39) is written as an expectation value with respect to the p.d.f. $P_{\mathbf{r}}$ for the configurations of symmetry-independent atoms in the basic-structure unit cell [(4.7)],

$$Q(u,v) = \int_V\cdots\int_V \exp[i(Au+Bv)]P_{\mathbf{r}}(\mathbf{r}_0^1,\ldots,\mathbf{r}_0^{N/K})\,\mathrm{d}\mathbf{r}_0^1\ldots\mathrm{d}\mathbf{r}_0^{N/K}, \tag{4.40}$$

with V being the volume of the basic-structure unit cell.

Using the *a priori* assumption of symmetry-independent atoms being uniformly distributed throughout the basic-structure unit cell, *i.e.* $P_{\mathbf{r}}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K}) = V^{-N/K}$ (a function independent of the average atomic positions), the characteristic function (4.40) becomes

$$Q(u,v) = V^{-N/K} \int_V \cdots \int_V \exp[i(Au + Bv)]\, \mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}. \tag{4.41}$$

In polar form, the structure factor is written as $F = |F| \exp(i\Phi)$, where the amplitude $|F|$ and phase Φ can also be considered as continuous random variables. By the introduction of polar coordinates $a = R\cos\varphi$, $b = R\sin\varphi$, $u = \rho\cos\xi$ and $v = \rho\sin\xi$, and using $P_{|F|,\Phi}(R,\varphi)\,\mathrm{d}R\,\mathrm{d}\varphi = P_{A,B}(a,b)\,\mathrm{d}a\,\mathrm{d}b$, the p.d.f. for $(|F|, \Phi)$ having the numerical values (R,φ) is obtained from (4.38) as [(4.8)]

$$\begin{aligned} P_{|F|,\Phi}(R,\varphi) &= (2\pi)^{-2} R \int_0^\infty \int_0^{2\pi} \exp[-iR\rho\cos(\xi - \varphi)] \times \\ &\qquad Q(\rho\cos\xi, \rho\sin\xi)\, \rho\, \mathrm{d}\rho\, \mathrm{d}\xi. \end{aligned} \tag{4.42}$$

Note that the polar-coordinate transformation $(A,B) \rightarrow (|F|, \Phi)$ introduces a factor R in (4.42) so that, for small values of the structure-factor amplitude, the p.d.f. [(4.13)] will be proportional to the structure-factor amplitude. This behavior of the p.d.f. is characteristic for non-phase-restricted reflections. It means that the diffraction pattern of the (incommensurately modulated) crystal will very likely contain many 'strong' reflections. A p.d.f. showing such behavior is called acentric.

The characteristic function (4.41) is evaluated as follows. For each configuration of the average atomic positions $\mathbf{r}_0^\mu$ of the symmetry-independent atoms in the basic-structure unit cell, the structure factor F is given by equation (4.1). By use of $F = A + iB$ and substitution of the polar coordinates, the argument of the exponent in (4.41) becomes

$$i\rho\epsilon \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} |g_k^\mu| f_k^\mu \cos\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + mv_4^k\right) + \theta_k^\mu - \xi\right]. \tag{4.43}$$

The summations can be taken out of the argument so that the exponent in (4.41) can be expressed as a multiple product of exponential functions:

$$\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} \exp\left\{i\rho\epsilon |g_k^\mu| f_k^\mu \cos\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + mv_4^k\right) + \theta_k^\mu - \xi\right]\right\}. \tag{4.44}$$

Using the identity [equation (8.511-4) of Gradshteyn & Ryzhik (1980)]

$$\exp(iz\cos\phi) = \sum_{n=-\infty}^{\infty} i^n J_n(z) \exp(in\phi), \tag{4.45}$$

where J_n is the nth-order Bessel function and $i = \exp(i\pi/2)$, this can be written as

$$\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon}\sum_{n^c_{\mu,k}=-\infty}^{\infty} J_{n^c_{\mu,k}}(\rho\epsilon|g^\mu_k|f^\mu_k)\times$$

$$\exp\left\{in^c_{\mu,k}\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}^\mu_0+\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\xi+\pi/2\right]\right\}. \qquad (4.46)$$

The multiple product can be taken inside the summation. The resulting expression for the exponent in (4.41) is then an N/ϵ-tuple sum over integers $n^c_{\mu,k}$, of the form [(4.9)]

$$\sum_{n^c_{1,1}=-\infty}^{\infty}\cdots\sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty}\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon}J_{n^c_{\mu,k}}(\rho\epsilon|g^\mu_k|f^\mu_k)\right]\times$$

$$\exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/\epsilon}n^c_{\mu,k}\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}^\mu_0+\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\xi+\pi/2\right]\right\}. \qquad (4.47)$$

By substitution of (4.47) for the exponent in (4.41), the characteristic function can be written as

$$Q(\rho\cos\xi,\rho\sin\xi)=\sum_{n^c_{1,1}=-\infty}^{\infty}\cdots\sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty}$$

$$\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon}J_{n^c_{\mu,k}}(\rho\epsilon|g^\mu_k|f^\mu_k)\right]\times$$

$$\exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/\epsilon}n^c_{\mu,k}\left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\xi+\pi/2\right]\right\}\times$$

$$\left\{\prod_{\mu=1}^{N/K}\prod_{j=1}^{3}\int_0^1\exp\left[2\pi i\left(\sum_{k=1}^{K/\epsilon}n^c_{\mu,k}\sum_{i=1}^{3}S_iR^k_{ij}\right)x^\mu_{0,j}\right]\mathrm{d}x^\mu_{0,j}\right\}. \qquad (4.48)$$

Here, $S_i = H_i + mq_i$ is the ith component of the diffraction vector $\mathbf{S} = \sum_{i=1}^{3} S_i\,\mathbf{a}^*_i$, where H_i is the ith (integer) component of a basic-structure reciprocal-lattice vector, q_i is the ith component of the modulation wave vector and m is the integer satellite index. The integration variable $x^\mu_{0,j}$ is the jth component of the average atomic position $\mathbf{r}^\mu_0 = \sum_{j=1}^{3} x^\mu_{0,j}\,\mathbf{a}_j$ and R^k_{ij} is the ijth component of the matrix R_k. The magnitude of the infinitesimal volume element $\mathrm{d}\mathbf{r}^\mu_0$ in (4.41), spanned by the vectors $\mathrm{d}x^\mu_{0,j}\,\mathbf{a}_j$ ($j = 1,2,3$), is equal to $V\,\mathrm{d}x^\mu_{0,1}\,\mathrm{d}x^\mu_{0,2}\,\mathrm{d}x^\mu_{0,3}$. Each integral now extends over one period (in the basic structure) along the $\mathbf{a}_j$ axes.

When performing the integration with respect to the components of the average atomic positions, one should be aware that, for main reflections, the components of $\mathbf{S}$ are all integers while, for satellite reflections, at least one of the components of $\mathbf{S}$ is not an integer. The integrals in (4.48) are then evaluated as

$$\int_0^1 \exp(2\pi i \alpha^c_{\mu,j} x^\mu_{0,j})\, \mathrm{d}x^\mu_{0,j} = h(\alpha^c_{\mu,j}) \exp(i\pi\alpha^c_{\mu,j}), \tag{4.49}$$

with the numbers $\alpha^c_{\mu,j}$ given by [(4.12)]

$$\alpha^c_{\mu,j} = \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} \left(\sum_{i=1}^{3} S_i R^k_{ij} \right) \tag{4.50}$$

and with the function h defined as [(4.11)]

$$h(z) = \begin{cases} 1 & (z = 0) \\ (\pi z)^{-1} \sin(\pi z) & (z \neq 0). \end{cases} \tag{4.51}$$

From (4.48), (4.49), (4.50) and (4.51), the expression for the characteristic function is finally obtained as [(4.10)]

$$\begin{aligned} Q(\rho\cos\xi, \rho\sin\xi) = & \sum_{n^c_{1,1}=-\infty}^{\infty} \cdots \sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty} \\ & \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \exp(i\pi\alpha^c_{\mu,j}) \right] \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n^c_{\mu,k}}(\rho\epsilon |g^\mu_k| f^\mu_k) \right] \times \\ & \exp\left\{ i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} \left[2\pi \left(\mathbf{H}\cdot\mathbf{v}_k + m v^k_4 \right) + \theta^\mu_k - \xi + \pi/2 \right] \right\}. \end{aligned} \tag{4.52}$$

Note that $h(\alpha^c_{\mu,j}) = 0$ if $\alpha^c_{\mu,j}$ is a nonzero integer. Therefore, a term in the multiple summation of (4.52) will be nonzero only if the $\alpha^c_{\mu,j}$ ($\mu = 1, \ldots, N/K$; $j = 1, 2, 3$) are zero or non-integer. For main reflections, the components of $\mathbf{S}$ are integers and $\alpha^c_{\mu,j}$ is always an integer too. Then, only terms contribute for which $\alpha^c_{\mu,j} = 0$ for all μ and j. For satellite reflections, there is no such condition because at least one of the coordinates of the diffraction vector is not an integer. However, terms in the multiple summation with some of the $\alpha^c_{\mu,j}$ not an integer and all others zero decrease rapidly in magnitude.

The p.d.f. $P_{|F|,\Phi}$ for the structure factor in polar form can be evaluated as follows. First, the exponent in (4.42) is expanded, using (4.45), to give

$$\exp\left[-i\rho R\cos(\xi - \varphi)\right] = \sum_{n_c=-\infty}^{\infty} J_{n_c}(\rho R) \exp\left[i n_c (\xi - \varphi + 3\pi/2)\right]. \tag{4.53}$$

Substitution of (4.53), together with expression (4.52) for the characteristic function, in (4.42) then gives

$$
\begin{aligned}
P_{|F|,\Phi}(R,\varphi) = (2\pi)^{-2} R \sum_{n^c_{1,1}=-\infty}^{\infty} \cdots \sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty} \sum_{n_c=-\infty}^{\infty} \\
\left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \exp(i\pi\alpha^c_{\mu,j})\right] \times \\
\left\{\int_0^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n^c_{\mu,k}}(\rho\epsilon|g^{\mu}_{k}|f^{\mu}_{k})\right] J_{n_c}(\rho R)\, \rho\, \mathrm{d}\rho\right\} \times \\
\exp\left\{i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} \left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k + m v_4^k\right) + \theta^{\mu}_{k} + \pi/2\right] + i n_c (3\pi/2 - \varphi)\right\} \times \\
\int_0^{2\pi} \exp\left[i\left(n_c - \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k}\right)\xi\right] \mathrm{d}\xi. \qquad (4.54)
\end{aligned}
$$

Because both n_c and the numbers $n^c_{\mu,k}$ are integers, the integral with respect to ξ in (4.54) is zero, except when

$$
n_c = \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k}. \qquad (4.55)
$$

It follows that precisely one term in the summation with respect to n_c gives a nonzero contribution. With n_c given by (4.55), the p.d.f. then becomes

$$
\begin{aligned}
P_{|F|,\Phi}(R,\varphi) \;=\; (2\pi)^{-1} R \sum_{n^c_{1,1}=-\infty}^{\infty} \cdots \sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty} \\
\left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \exp(i\pi\alpha^c_{\mu,j})\right] \times \\
\left\{\int_0^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n^c_{\mu,k}}(\rho\epsilon|g^{\mu}_{k}|f^{\mu}_{k})\right] J_{n_c}(\rho R)\, \rho\, \mathrm{d}\rho\right\} \times \\
\exp\left\{i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} \left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k + m v_4^k\right) + \theta^{\mu}_{k} - \varphi\right]\right\}. \qquad (4.56)
\end{aligned}
$$

To show that the p.d.f. in (4.56) is a real function, consider what happens if, in a single term in the multiple summation, all integers $n^c_{\mu,k}$ are reversed in sign. By use of a property of Bessel functions [equation (8.404-2) of Gradshteyn & Ryzhik (1980)],

$$J_{-n}(z) = (-1)^n J_n(z), \tag{4.57}$$

one can see, with the help of (4.55), that the integral with respect to ρ does not change sign. Neither does the function h, given by (4.51), although its argument changes sign. But the arguments of the exponential functions do reverse their signs. This means that for each term in (4.56) with given integers $n^c_{\mu,k}$, there exists a corresponding term with integers $-n^c_{\mu,k}$, being its complex conjugate. Note that the term with integers $n^c_{\mu,k} = 0$, for all μ and k, is a real function by itself. It follows that all the imaginary parts in the multiple summation of (4.56) cancel, causing the p.d.f. to be a real function:

$$\begin{aligned} P_{|F|,\Phi}(R,\varphi) = (2\pi)^{-1} R \sum_{n^c_{1,1}=-\infty}^{\infty} \cdots \sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \right] \times \\ \left\{ \int_0^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n^c_{\mu,k}}(\rho\epsilon|g^\mu_k|f^\mu_k) \right] J_{n_c}(\rho R)\, \rho \, \mathrm{d}\rho \right\} \times \\ \cos\left(\sum_{\mu=1}^{N/K} \left\{ \pi \sum_{j=1}^{3} \alpha^c_{\mu,j} + \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} \left[2\pi \left(\mathbf{H}\cdot\mathbf{v}_k + m v_4^k \right) + \theta^\mu_k - \varphi \right] \right\} \right). \end{aligned} \tag{4.58}$$

Finally, the p.d.f. $P_{|F|}$ for the structure-factor amplitude $|F|$ having the numerical value R is obtained by integration with respect to the phase of the structure factor, *i.e.*

$$P_{|F|}(R) = \int_0^{2\pi} P_{|F|,\Phi}(R,\varphi)\, \mathrm{d}\varphi. \tag{4.59}$$

Only those terms in (4.58) for which the condition

$$\sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n^c_{\mu,k} = 0 \tag{4.60}$$

is fulfilled will give a nonzero contribution to the integral in (4.59). In addition, from (4.55) and condition (4.60), it follows that $n_c = 0$. The p.d.f. $P_{|F|}$ can then be written as

$$\begin{aligned} P_{|F|}(R) \;=\; R \sum_{n^c_{1,1}=-\infty}^{\infty} \cdots \sum_{n^c_{N/K,K/\epsilon}=-\infty}^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^c_{\mu,j}) \right] \times \end{aligned}$$

$$\left\{\int_0^\infty \left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon} J_{n^c_{\mu,k}}(\rho\epsilon|g^\mu_k|f^\mu_k)\right] J_0(\rho R)\,\rho\,\mathrm{d}\rho\right\} \times$$

$$\cos\left(\sum_{\mu=1}^{N/K}\left\{\pi\sum_{j=1}^{3}\alpha^c_{\mu,j}+\sum_{k=1}^{K/\epsilon} n^c_{\mu,k}\left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k+mv_4^k\right)+\theta^\mu_k\right]\right\}\right). \quad (4.61)$$

This leads directly to (4.13) and (4.14).

Phase-restricted reflections

The structure factor of a phase-restricted reflection, given by (4.4), is again a complex function of the independent continuous random variables $\mathbf{r}^\mu_0$. However, in this case, the phase Φ of the structure factor is restricted to two values, φ_1 and $\varphi_1+\pi$, with φ_1 given by (4.5), and thus represents a discrete random variable. Only the amplitude of the structure factor is a continuous random variable. A phase shift can be applied to the structure factor F', given by (4.4), so that the new structure factor $F = F'\exp(-i\varphi_1)$ is a real function. The pair of random variables $(|F'|,\Phi)$ can then be replaced by a single continuous random variable F, the new structure factor itself, which can assume both positive and negative values. Because $|F| = |F'|$, the p.d.f. for the structure-factor amplitude is the same when derived from F instead of F'. In general, the p.d.f. P_F for F having the numerical value c can be written as a one-dimensional Fourier transform [(4.16)]:

$$P_F(c) = (2\pi)^{-1}\int_{-\infty}^{\infty}\exp(-icw)Q(w)\,\mathrm{d}w. \quad (4.62)$$

Because F can be positive as well as negative, the p.d.f. $P_{|F|}$ for the structure-factor amplitude $|F|$ having the numerical value R is obtained from (4.62) as [(4.17)]

$$\begin{aligned} P_{|F|}(R) &\equiv P_F(-R)+P_F(R) \quad (R\neq 0) \\ &= \pi^{-1}\int_{-\infty}^{\infty}\cos(wR)Q(w)\,\mathrm{d}w. \end{aligned} \quad (4.63)$$

Note that in contrast to the derivation of the p.d.f. for the structure-factor amplitude of non-phase-restricted reflections [(4.13)], polar-coordinate transformations cannot be used here because (4.62) is a one-dimensional Fourier transform. Thus, for small values of the structure-factor amplitude, instead of being proportional to the structure-factor amplitude, the p.d.f. [(4.21)] will be of order unity. This behavior of the p.d.f. is characteristic for phase-restricted reflections. It means that, compared to the acentric case, the diffraction pattern of the (incommensurately modulated) crystal will very likely contain many 'weak' reflections. A p.d.f. showing this behavior is called centric.

The characteristic function Q is by definition the inverse Fourier transform of P_F. Consequently, the characteristic function can be written as an expectation value with respect to the p.d.f. P_F:

$$Q(w) = \langle \exp(iFw) \rangle . \tag{4.64}$$

Because P_F is unknown, the characteristic function (4.64) is written as an expectation value with respect to the p.d.f. $P_{\mathbf{r}}$ for the configurations of symmetry-independent atoms in the basic-structure unit cell [(4.18)]:

$$Q(w) = \int_V \cdots \int_V \exp(iFw) P_{\mathbf{r}}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K}) \, \mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}. \tag{4.65}$$

Using the *a priori* assumption of symmetry-independent atoms being uniformly distributed throughout the basic-structure unit cell, *i.e.* $P_{\mathbf{r}}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K}) = V^{-N/K}$ (a function independent of the average atomic positions), the characteristic function (4.65) becomes

$$Q(w) = V^{-N/K} \int_V \cdots \int_V \exp(iFw) \, \mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}. \tag{4.66}$$

The characteristic function is evaluated as follows. For each configuration of the average atomic positions $\mathbf{r}_0^\mu$ of the symmetry-independent atoms in the basic-structure unit cell, the structure factor F' is given by (4.4). Using $F = F' \exp(-i\varphi_1)$, the exponent in (4.66) becomes

$$\exp\left\{ 2iw\epsilon \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} |g_k^\mu| f_k^\mu \cos\left[2\pi \left(\mathbf{S} \cdot \mathsf{R}_k \cdot \mathbf{r}_0^\mu + \mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \varphi_1 \right] \right\}. \tag{4.67}$$

Comparing the argument of the exponent in (4.67) with a similar expression for non-phase-restricted reflections given by (4.43), one can see that in (4.67), the summation with respect to the symmetry operators counts only half the number of symmetry operators while the symmetry-enhancement factor ϵ has been replaced by 2ϵ. Also note that in (4.43), there is a variable ξ which, in (4.67), is replaced by the fixed phase φ_1 given by (4.5). These differences are directly related to the differences between the structure factors (4.1) and (4.4), caused by factoring out a symmetry operator which transforms the diffraction vector $\mathbf{S}$ into $-\mathbf{S}$.

The multiple summation in (4.67) can be taken out of the argument, resulting in the following multiple product of exponential functions:

$$\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} \exp\left\{ 2iw\epsilon |g_k^\mu| f_k^\mu \cos\left[2\pi \left(\mathbf{S} \cdot \mathsf{R}_k \cdot \mathbf{r}_0^\mu + \mathbf{H} \cdot \mathbf{v}_k + m v_4^k \right) + \theta_k^\mu - \varphi_1 \right] \right\}. \tag{4.68}$$

Using (4.45), this can be written as

$$\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/(2\epsilon)}\sum_{n^d_{\mu,k}=-\infty}^{\infty} J_{n^d_{\mu,k}}(2w\epsilon|g^\mu_k|f^\mu_k)\times$$

$$\exp\left\{in^d_{\mu,k}\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}^\mu_0+\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\varphi_1+\pi/2\right]\right\}. \tag{4.69}$$

The multiple product can be taken inside the summation. Because there are only half as many integers $n^d_{\mu,k}$ as integers $n^c_{\mu,k}$ in (4.48), the resulting expression for the exponent in (4.66) is an $N/(2\epsilon)$-tuple sum over integers $n^d_{\mu,k}$, of the form

$$\sum_{n^d_{1,1}=-\infty}^{\infty}\cdots\sum_{n^d_{N/K,K/(2\epsilon)}=-\infty}^{\infty}\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/(2\epsilon)} J_{n^d_{\mu,k}}(2w\epsilon|g^\mu_k|f^\mu_k)\right]\times$$

$$\exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k}\left[2\pi\left(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}^\mu_0+\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\varphi_1+\pi/2\right]\right\}. \tag{4.70}$$

By substitution of (4.70) for the exponent in (4.66), the characteristic function can be written, similar to (4.48), as

$$\begin{aligned} Q(w) \;=\; & \sum_{n^d_{1,1}=-\infty}^{\infty}\cdots\sum_{n^d_{N/K,K/(2\epsilon)}=-\infty}^{\infty}\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/(2\epsilon)} J_{n^d_{\mu,k}}(2w\epsilon|g^\mu_k|f^\mu_k)\right]\times \\ & \exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k}\left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k+mv^k_4\right)+\theta^\mu_k-\varphi_1+\pi/2\right]\right\}\times \\ & \left\{\prod_{\mu=1}^{N/K}\prod_{j=1}^{3}\int_0^1\exp\left[2\pi i\left(\sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k}\sum_{i=1}^{3} S_i R^k_{ij}\right)x^\mu_{0,j}\right]\mathrm{d}x^\mu_{0,j}\right\}. \end{aligned} \tag{4.71}$$

The integrals in (4.71), which are of the same type as those in (4.48), are then evaluated as

$$\int_0^1\exp(2\pi i\alpha^d_{\mu,j}x^\mu_{0,j})\,\mathrm{d}x^\mu_{0,j}=h(\alpha^d_{\mu,j})\exp(i\pi\alpha^d_{\mu,j}), \tag{4.72}$$

with the function h given by (4.51) and the numbers $\alpha^d_{\mu,j}$ given by [(4.20)]

$$\alpha^d_{\mu,j}=\sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k}\left(\sum_{i=1}^{3} S_i R^k_{ij}\right). \tag{4.73}$$

The numbers $\alpha^d_{\mu,j}$ have the same meaning as the numbers $\alpha^c_{\mu,j}$ given by (4.50). The difference lies in the number of symmetry operators involved in their definitions.

From (4.71), (4.72), (4.73) and (4.51), the expression for the characteristic function is finally obtained as [(4.19)]

$$Q(w) = \sum_{n^d_{1,1}=-\infty}^{\infty} \cdots \sum_{n^d_{N/K,K/(2\epsilon)}=-\infty}^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^d_{\mu,j}) \exp(i\pi\alpha^d_{\mu,j})\right] \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n^d_{\mu,k}}(2w\epsilon|g^\mu_k|f^\mu_k)\right] \times \exp\left\{i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k}\left[2\pi\left(\mathbf{H}\cdot\mathbf{v}_k + mv^k_4\right) + \theta^\mu_k - \varphi_1 + \pi/2\right]\right\}. \quad (4.74)$$

This expression can be used to derive a useful property of the characteristic function. First, all integers $n^d_{\mu,k}$ in (4.74) are replaced by $-n^d_{\mu,k}$. This transformation is equivalent to a rearrangement of all the terms in the multiple summation and therefore does not change the characteristic function. The effect of this transformation on right-hand side of (4.74) is to change the sign of the arguments in the exponential functions while the Bessel functions change according to (4.57). The function h, given by (4.51), is an even function and does not change. In the next step, the variable w is replaced by $-w$. This only influences the Bessel functions, which change their signs according to [equation (8.476-1) of Gradshteyn & Ryzhik (1980)]

$$J_n(-x) = (-1)^n J_n(x), \quad (4.75)$$

thereby canceling the effect of the previous transformation on the multiple product of Bessel functions. Therefore, the final result of these transformations can be written as

$$Q(-w) = Q^*(w), \quad (4.76)$$

where * denotes the complex conjugate.

To obtain the p.d.f. $P_{|F|}$ for the structure-factor amplitude, the integral in (4.63) can be rewritten, using a simple integral transformation and (4.76), to give

$$P_{|F|}(R) = \pi^{-1} \int_0^\infty [Q(w) + Q^*(w)] \cos(wR)\, dw, \quad (4.77)$$

which shows that the p.d.f. is a real function. Substitution of (4.74) in (4.77) then gives

the following result for the p.d.f. of the structure-factor amplitude:

$$P_{|F|}(R) = 2\pi^{-1} \sum_{n^d_{1,1}=-\infty}^{\infty} \cdots \sum_{n^d_{N/K,K/(2\epsilon)}=-\infty}^{\infty} \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha^d_{\mu,j}) \right] \times$$

$$\left\{ \int_0^\infty \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n^d_{\mu,k}}(2w\epsilon|g^\mu_k||f^\mu_k|) \right] \cos(wR)\,\mathrm{d}w \right\} \times$$

$$\cos\left(\sum_{\mu=1}^{N/K} \left\{ \pi \sum_{j=1}^{3} \alpha^d_{\mu,j} + \sum_{k=1}^{K/(2\epsilon)} n^d_{\mu,k} \left[2\pi \left(\mathbf{H}\cdot\mathbf{v}_k + mv^k_4 \right) + \theta^\mu_k - \varphi_1 + \pi/2 \right] \right\} \right). \quad (4.78)$$

This leads directly to (4.21) and (4.22). Note that a condition like (4.60) for non-phase-restricted reflections does not exist for phase-restricted reflections.

References

AALST, W. VAN, HOLLANDER, J. DEN, PETERSE, W. J. A. M. & WOLFF, P. M. DE (1976). *Acta Cryst.* B**32**, 47–58.

BAUDOUR, J. L. & SANQUER, M. (1983). *Acta Cryst.* B**39**, 75–84.

CASTLEDEN, I. R. (1987). *Acta Cryst.* A**43**, 384–393.

GIACOVAZZO, C. (1980). *Direct Methods in Crystallography.* London: Academic.

GRADSHTEYN, I. S. & RYZHIK, M. (1980). *Table of Integrals, Series, and Products.* London: Academic.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HAO, Q., LIU, Y.-W. & FAN, H.-F. (1987). *Acta Cryst.* A**43**, 820–824.

HAUPTMAN, H. & KARLE, J. (1952). *Acta Cryst.* **5**, 48–59.

HAUPTMAN, H. & KARLE, J. (1953). *Acta Cryst.* **6**, 136–141.

JANNER, A., JANSSEN, T. & WOLFF, P. M. DE (1983). *Acta Cryst.* A**39**, 658–666.

KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 131–135.

KARLE, J & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

LAM, E. J. W., BEURSKENS, P. T. & SMAALEN, S. VAN (1992). *Solid State Commun.* **82**, 345–349.

PESCHAR, R. (1987). PhD thesis. Univ. of Amsterdam, The Netherlands.

PETŘÍČEK, V., COPPENS, P. & BECKER, P. (1985). *Acta Cryst.* A**41**, 478–483.

SCHUTTE, W. J. (1990). PhD thesis. Univ. of Groningen, The Netherlands.

SHMUELI, U., WEISS, G. H. & KIEFER, J. E. (1985). *Acta Cryst.* A**41**, 55–59.

SRINIVASAN, R. & PARTHASARATHY, S. (1976). *Some Statistical Applications in X-ray Crystallography. International Series in Natural Philosophy*, Vol. 83. Oxford: Pergamon.

STEURER, W. (1987). *Acta Cryst.* A**43**, 36–42.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.

WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258 261.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.

WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625–636.

YAMAMOTO, A. (1982). *Acta Cryst.* A**38**, 87–92.

5

Direct Methods for Incommensurately Modulated Structures. On the Applicability of Normalized Structure Factors*

Abstract

The recently defined normalized structure factors [Lam, Beurskens & van Smaalen (1993), *Acta Cryst.* A**49**, 709–721] have been subjected to extensive tests regarding their applicability in direct methods for phase determination. It is shown that the probability distribution associated with the structure invariant $\varphi(-\mathbf{H})+\varphi(\mathbf{H}')+\varphi(\mathbf{H}-\mathbf{H}')$, where $\mathbf{H}$ and $\mathbf{H}'$ represent main and/or satellite reflections, approximately has the same functional form as the Cochran distribution. In general, triplet relations involving satellite reflections are less reliable than relations involving main reflections only. In addition, refinement of phases by the multidimensional Sayre equation [Hao, Liu & Fan (1987), *Acta Cryst.* A**43**, 820–824] generally shows a better convergence when the newly defined normalized structure factors are used instead of ordinary structure factors.

*A more complete manuscript is in preparation and will be published as: Gelder, R. de, Lam, E. J. W., Israel, R., Beurskens, P. T., Smaalen, S. van, Fu, Z.-Q. & Fan, H. F. (1995).

5.1 Introduction

Direct methods for solving the phase problem in X-ray crystallography have been extended to incommensurately modulated structures by Hao, Liu & Fan (1987). Recently, normalized structure factors (E) were defined for main reflections and satellite reflections of modulated structures (Lam, Beurskens & van Smaalen, 1992, 1993, 1994). The conventional definition of normalized structure factors is

$$E(\mathbf{H}) = F(\mathbf{H})/g(|\mathbf{H}|), \tag{5.1}$$

where $g(|\mathbf{H}|)$ is a real function which compensates for the decrease in the scattering power of the atoms with increasing $|\mathbf{H}|$. This includes the effect of the overall isotropic temperature factor. This definition was extended to modulated structures by introduction of a modified expression for the function $g(|\mathbf{H}|)$ which now includes overall modulation effects. Different expressions for $g(|\mathbf{H}|)$ were required for main reflections and satellites. It was shown that the statistical distributions of the magnitudes of the newly defined E values obey similar distributions as known for nonmodulated crystals. It is not at all trivial or obvious, however, that normalized structure factors of main or satellite reflections should have the same statistical properties regarding phase relations as E values of conventional (nonmodulated) structures. In the present paper, we explore the meaning of the normalized structure factors for modulated structures. The probability distributions for triplet-phase sums are calculated for a series of modulated structures and compared with the Cochran distribution (Cochran & Woolson, 1955; Cochran, 1955). In addition, for several modulated structures, phases of satellite reflections were also estimated employing the multidimensional Sayre equation (Hao, Liu & Fan, 1987) and compared to values calculated from the published structural models.

5.2 The three-phase structure invariant

The most frequently used phase relation in direct methods for solving (nonmodulated) crystal structures is the three-phase structure invariant, *i.e.* the phase of the triple product $E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')$ or $F(-\mathbf{H})F(\mathbf{H}')F(\mathbf{H}-\mathbf{H}')$. The phase sum Φ of the triplet,

$$\Phi = \varphi(-\mathbf{H}) + \varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}'), \tag{5.2}$$

is independent of the choice of the space-group origin and is likely to be close to zero for large magnitudes of $|E(\mathbf{H})|$, $|E(\mathbf{H}')|$ and $|E(\mathbf{H}-\mathbf{H}')|$. For noncentrosymmetric structures,

this leads to the following phase relation:

$$\varphi(\mathbf{H}) \approx \varphi(\mathbf{H}') + \varphi(\mathbf{H} - \mathbf{H}'), \tag{5.3}$$

where the $\approx$ sign means 'probably close to'. Here, it is assumed that Friedel's law applies, *i.e.* $\varphi(\mathbf{H}) = -\varphi(-\mathbf{H})$. The distribution of $\varphi(\mathbf{H})$ is given by (Cochran, 1955)

$$P[\varphi(\mathbf{H})] = \frac{1}{2\pi I_0[\kappa(\mathbf{H},\mathbf{H}')]} \exp\left\{\kappa(\mathbf{H},\mathbf{H}')\cos[\varphi(\mathbf{H}) - \varphi(\mathbf{H}') - \varphi(\mathbf{H} - \mathbf{H}')]\right\}, \tag{5.4}$$

where I_n is a modified Bessel function of the first kind and

$$\kappa(\mathbf{H},\mathbf{H}') = 2C|E(\mathbf{H})E(\mathbf{H}')E(\mathbf{H} - \mathbf{H}')| \tag{5.5}$$

with

$$C = \frac{\sum_{\mu=1}^{N} Z_\mu^3}{\left(\sum_{\mu=1}^{N} Z_\mu^2\right)^{3/2}}. \tag{5.6}$$

Here, Z_μ is the atomic number of atom μ and the summations extend over all atoms (N) in the unit cell. Note that for equal-atom structures, $C = N^{-1/2}$. The standard deviation σ of $\varphi(\mathbf{H})$ can be obtained from (Karle & Karle, 1966)†

$$\sigma^2(\kappa) = \frac{\pi^2}{3} + \frac{4}{I_0(\kappa)}\left[\sum_{n=1}^{\infty} \frac{I_{2n}(\kappa)}{(2n)^2} - \sum_{n=0}^{\infty} \frac{I_{2n+1}(\kappa)}{(2n+1)^2}\right]. \tag{5.7}$$

Distribution (5.4) shows a maximum at $\varphi(\mathbf{H}) = \varphi(\mathbf{H}') + \varphi(\mathbf{H} - \mathbf{H}')$. The width of this peak decreases with increasing κ which means that the estimate (5.3) for $\varphi(\mathbf{H})$ becomes more reliable. This implies that σ is a monotonously decreasing function for increasing κ. In case of centrosymmetric structures, phases are restricted to 0 and π and relation (5.3) becomes a sign relation:

$$\mathrm{sign}(\mathbf{H}) \simeq \mathrm{sign}(\mathbf{H}')\,\mathrm{sign}(\mathbf{H} - \mathbf{H}'). \tag{5.8}$$

where the $\simeq$ sign means 'probably equal to'. According to Cochran & Woolfson (1955), the probability that this sign relation is correct, is given by

$$P^+(x) = \frac{1}{2} + \frac{1}{2}\tanh(x), \tag{5.9}$$

where $x = \kappa/2$ with κ given by (5.5). Analogously to relation (5.3), the chance that the sign relation (5.8) is correct increases with increasing κ.

†Equation 3.33 of Karle & Karle (1966) erroneously contains a plus sign before the second summation.

Incommensurately modulated structures have diffraction patterns that consist of main reflections and satellite reflections. These two different types of reflections lead to different types of phase relations. For noncentrosymmetric modulated crystals, the following phase relations can be obtained from (5.3):

$$\varphi(\mathbf{H}_{\text{main}}) \approx \varphi(\mathbf{H}'_{\text{main}}) + \varphi(\mathbf{H}_{\text{main}} - \mathbf{H}'_{\text{main}}), \tag{5.10}$$

$$\varphi(\mathbf{H}_{\text{sat}}) \approx \varphi(\mathbf{H}'_{\text{main}}) + \varphi(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{main}}), \tag{5.11}$$

$$\varphi(\mathbf{H}_{\text{sat}}) \approx \varphi(\mathbf{H}'_{\text{sat}}) + \varphi(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{sat}}). \tag{5.12}$$

For centrosymmetric modulated structures, one can distinguish the following expressions from (5.8):

$$\text{sign}(\mathbf{H}_{\text{main}}) \simeq \text{sign}(\mathbf{H}'_{\text{main}})\,\text{sign}(\mathbf{H}_{\text{main}} - \mathbf{H}'_{\text{main}}), \tag{5.13}$$

$$\text{sign}(\mathbf{H}_{\text{sat}}) \simeq \text{sign}(\mathbf{H}'_{\text{main}})\,\text{sign}(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{main}}), \tag{5.14}$$

$$\text{sign}(\mathbf{H}_{\text{sat}}) \simeq \text{sign}(\mathbf{H}'_{\text{sat}})\,\text{sign}(\mathbf{H}_{\text{sat}} - \mathbf{H}'_{\text{sat}}). \tag{5.15}$$

The subscripts 'main' and 'sat' refer to main reflections $(h, k, l, 0)$ and satellite reflections $(h, k, l, m \neq 0)$, respectively. As we are mainly interested in phase determination of first order satellites, only test results regarding sign relations (5.11) and (5.14) for first-order satellites ($|m| = 1$) are considered. Results for (5.10) and (5.13) are also presented for comparison. In analogy to phase relations for nonmodulated structures, it may be expected that the probability that the triplet relations [(5.10)–(5.15)] are correct, increases for increasing values of $|E(-\mathbf{H})|$, $|E(\mathbf{H}')|$ and $|E(\mathbf{H} - \mathbf{H}')|$. In this paper, we present numerical tests for this hypothesis.

5.3 Numerical results

Numerical tests have been performed with structure factors from a number of compounds with a one-dimensional displacive modulation. In all cases, only main reflections and first-order satellites were used. Here, we present four typical cases. Two data sets were obtained for experimentally determined centrosymmetric structures (Table 5.1), but instead of the measured intensities, calculated structure factors were employed, thus avoiding complications due to incomplete data sets as published in the literature. Further tests were done for two simulated test structures having displacive modulations with random amplitudes and directions (Table 5.1): a centrosymmetric structure (C2) and a noncentrosymmetric structure (A2). These structures were designed to fulfill the requirement of a random distribution of atoms in the unit cell (Cochran & Woolfson, 1955; Cochran, 1955).

Table 5.1. Test structures having an incommensurate one-dimensional displacive modulation.

The notation for the (3 + 1)-dimensional superspace groups follows the nomenclature of Janssen, Janner, Looijenga-Vos & de Wolff (1992), however, nonstandard settings are used for Na_2CO_3 and K_2SeO_4. The overall modulation amplitude (U) is given by Equation (14) of Lam, Beurskens & van Smaalen (1992).

Compound	Superspace group	U(Å)	Reference
Na_2CO_3	$C2/m(\alpha,0,\gamma)0s$	0.386	van Aalst *et al.* (1976)
K_2SeO_4	$Pnam(\alpha,0,0)0ss$	0.096	Yamada & Ikeda (1984)
C2	$P\bar{1}(\alpha,\beta,\gamma)$	0.2	Lam, Beurskens & van Smaalen (1993)
A2	$P1(\alpha,\beta,\gamma)$	0.2	Lam, Beurskens & van Smaalen (1993)

For centrosymmetric structures, the dependency of P^+ as function of x was calculated by determining the ratio of correct sign relations $\text{sign}(\mathbf{H}) = \text{sign}(\mathbf{H}')\,\text{sign}(\mathbf{H}-\mathbf{H}')$ *versus* the total number of sign relations at a given value of x. For the noncentrosymmetric structure, the differences between the phases calculated from the structural model and the estimated phases, $\varphi(\mathbf{H}) = \varphi(\mathbf{H}') + \varphi(\mathbf{H}-\mathbf{H}')$, were averaged to obtain a value for σ at a given value of κ. The left-hand sides of Figures 5.1–5.4 show results for triplet relations among main reflections only [(5.13) for centrosymmetric structures, (5.10) for the noncentrosymmetric structure]. The right-hand sides of these figures show results for triplet relations involving both satellite and main reflections [(5.14) for centrosymmetric structures, (5.11) for the noncentrosymmetric structure]. In Figures 5.1, 5.2 and 5.3, the curve for the theoretical Cochran distribution [(5.9)] is presented together with a fit of the Cochran distribution to the experimental data points, where the constant C [(5.6)] has been used as a variable fitting parameter. For the noncentrosymmetric structure, the curve for the theoretical standard deviation [(5.7)] is presented in Figure 5.4 together with a fit of the standard deviation to the experimental data points, again with C as the fitting parameter.

For Na_2CO_3 (see Figure 5.1), it is seen that the experimental curve for triplet relations involving main reflections only is above the Cochran curve, which is caused by a nonrandom distribution of atoms in the average unit cell (atoms at special positions, noncrystallographic centers of symmetry and/or special types of displacive modulation). Although the experimental curve, involving main and satellite reflections, follows the Cochran curve rather accurately, it is below the corresponding curve for triplet relations involving main reflections only. This means that relation (5.14) is less reliable than relation (5.13).

For K_2SeO_4 (see Figure 5.2), the experimental curve for triplet relations involving main reflections only is above the Cochran curve while the curve involving triplet relations for main and satellite reflections is considerably below the Cochran curve.

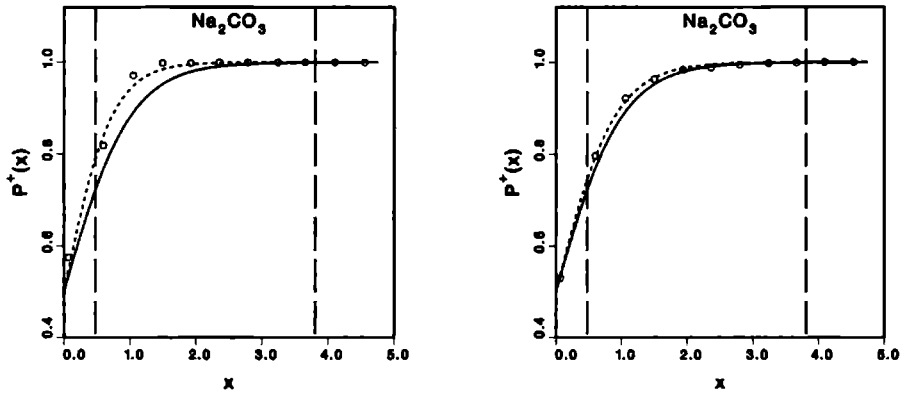


Figure 5.1. Probability distribution $P^+(x)$ for structure Na_2CO_3. Circles represent experimental values. Solid curves represent the theoretical distribution according to Cochran. Dashed curves represent the fitted curve through the experimental points. Vertical lines are drawn at values of x where $|E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')|^{1/3}$ is equal to 1 3 or 2.6. Left: Probability distribution $P^+(x)$ associated with sign relation (5.13), *i.e.* for main reflections only. Right: Probability distribution $P^+(x)$ associated with sign relation (5 14), i.e. relations involving main and satellite reflections.

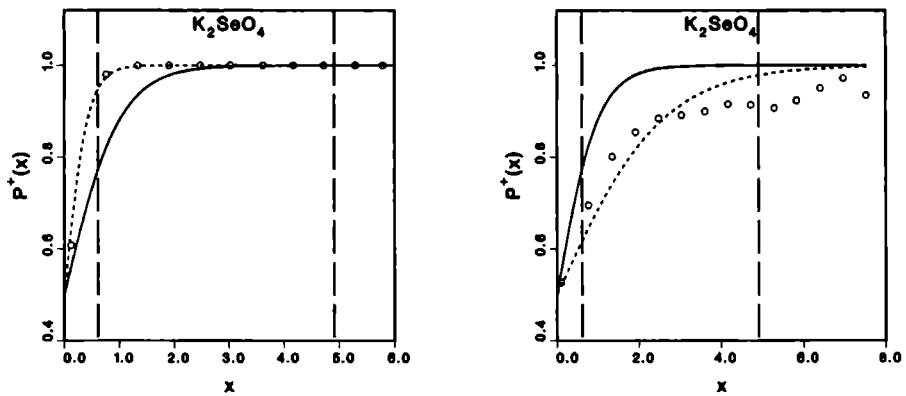


Figure 5.2. Test structure K_2SeO_4. See Figure 5.1 for explanation.

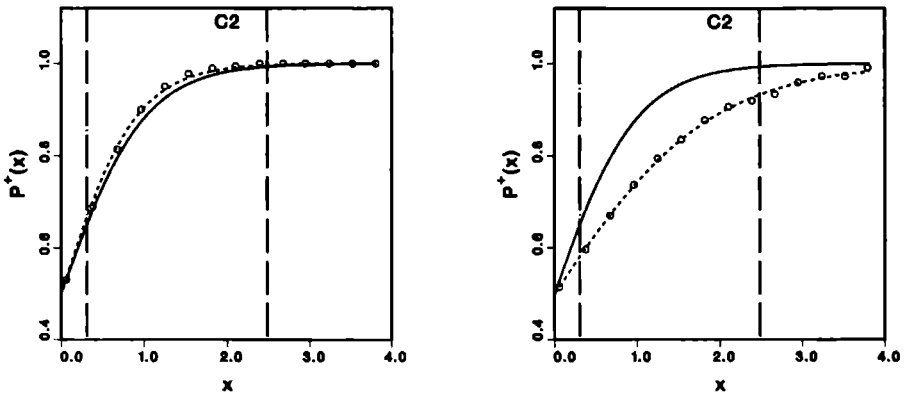


Figure 5.3. Test structure C2. See Figure 5.1 for explanation.

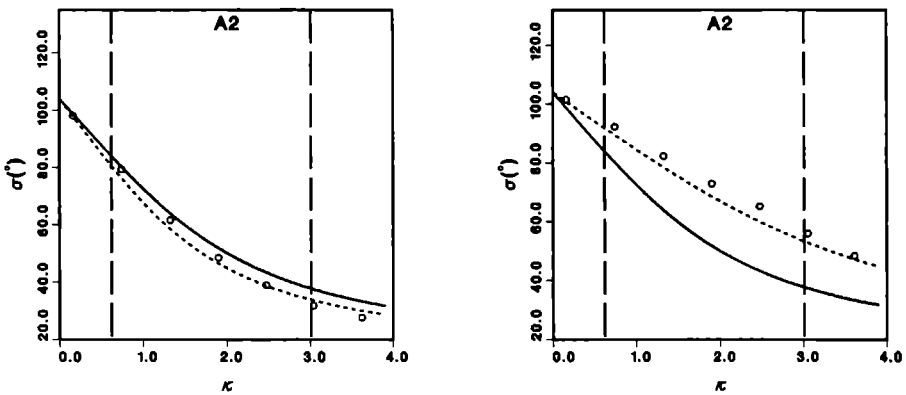


Figure 5.4. Standard deviation $\sigma(\kappa)$ for structure A2. Circles represent experimental values. Solid curves represent the theoretical distribution [(5 7)]. Dashed curves represent the fitted curve through the experimental points Vertical lines are drawn at values of κ where $|E(-\mathbf{H})E(\mathbf{H}')E(\mathbf{H}-\mathbf{H}')|^{1/3}$ is equal to 1 3 or 2.2 Left. Standard deviation $\sigma(\kappa)$ associated with phase relation (5.10), *i.e.* for main reflections only. Right: Standard deviation $\sigma(\kappa)$ associated with phase relation (5.11), i.e. relations involving main and satellite reflections. Note that here, σ is given in degrees while σ calculated from (5.7) is in radians.

For the random test structure C2 (see Figure 5.3), the main reflections give a distribution which properly follows the Cochran distribution but, again, the distribution for triplets involving main and satellite reflections is below the Cochran curve.

For the noncentrosymmetric random test structure A2 (see Figure 5.4), the standard deviations for triplet relations involving main reflections only are below the theoretically expected curve. The standard deviations for triplet relations involving main and satellite reflections are above this curve. This also indicates that triplet relations involving main and satellite reflections are less reliable than triplet relations involving main reflections only.

Note that the fitted curves are in good agreement with the experimental curves.

5.4 The multidimensional Sayre equation

To examine the refinement of satellite phases, employing normalized structure factors (E) instead of ordinary structure factors (F), a number of tests were performed with the program *DIMS* (Fu & Fan, 1994). This program employs the full Sayre equation for incommensurately modulated structures (Hao, Liu & Fan, 1987),

$$F(\mathbf{H}_{\rm sat}) = \Theta(\mathbf{H}_{\rm sat}) \sum_{\mathbf{H}_{\rm main}} F(\mathbf{H}_{\rm main}) F(\mathbf{H}_{\rm sat} - \mathbf{H}_{\rm main}), \tag{5.16}$$

to refine the phases of the satellite reflections using calculated phases for the main reflections and random phases for the satellites.

Tests were performed for a number of known centrosymmetric incommensurately modulated structures (see Table 5.1). The program *DIMS* was used to phase the first-order satellites given the known phases of the main reflections. In each test, the phases (signs) of the largest (normalized) structure factors were calculated and compared to their correct values calculated from the published structural model. Increasing the number of main or satellite reflections causes reflections with lower (normalized) structure-factor amplitudes to participate in the refinement by the multidimensional Sayre equation. In order to avoid complications due to incomplete data sets, as published in the literature, calculated structure factors were used instead of measured X-ray diffraction intensities.

Test results for Na_2CO_3 are given in Table 5.2. As can be seen, the use of E values instead of F values results in a smaller number of incorrectly determined phases. Increasing the number of main reflections, which means increasing the amount of reliable input phases, clearly shows that for E values, the number of incorrectly determined phases decreases. A similar decrease for F values could not be observed. Increasing the number of

Table 5.2. Test results from *DIMS* for compound Na_2CO_3.

Columns 2–9 show the number of phases incorrectly determined by the program *DIMS* using different numbers of main and satellite reflections. Columns E: results obtained by using normalized structure factors. Columns F: results obtained by using ordinary structure factors.

Number of satellites	100 main reflections		300 main reflections		500 main reflections		1000 main reflections	
	E	F	E	F	E	F	E	F
200	0	2	0	2	0	2	0	2
400	3	7	0	8	0	7	0	12
600	24	24	15	28	11	27	5	29
800	58	61	44	62	38	64	21	63
1000	91	123	74	138	64	126	41	112

satellite reflections leads to more phase errors for E values and, to a larger extent, also for F values. Apparently, more satellite reflections having a weak (normalized) structure-factor amplitude are phased incorrectly. Similar results were obtained for the other test structures.

5.5 Concluding remarks

All test structures show probability distributions for the triplet-phase relation that more or less follow the shape of the Cochran distribution. Although no mathematical prove is given, the conclusion is reached that the meaning and behavior of $|E|$ values for incommensurately modulated structures, when considering the triplet-phase relation, conform the meaning and behaviour of $|E|$ values for nonmodulated structures. The reliability for triplet-phase relations involving main and satellite reflections is slightly less compared to that of triplet-phase relations involving main reflections only (for equal κ). However, the phase problem for the satellite reflections may still be solved using procedures based on the triplet-phase relation. In general, refinement of satellite phases by use of the multidimensional Sayre equation results in fewer phase errors when E values are used instead of F values.

Further investigations regarding an adjustment of the constant C [in (5.5)] to obtain a more reliable estimate of the triplet probabilities are in progress. In particular, we are interested in the relation between the fitted parameter C and the overall modulation amplitude U.

References

Aalst, W. van, Hollander, J. den, Peterse, W. J. A. M. & Wolff, P. M. de (1976). *Acta Cryst.* B**32**, 47–58.

Cochran, W. (1955). *Acta Cryst.* **8**, 473–478.

Cochran, W. & Woolfson, M. M. (1955). *Acta Cryst.* **8**, 1–12.

Fu, Z.-Q. & Fan, H.-F. (1994). *J. Appl. Cryst.* **27**, 124–127.

Hao, Q., Liu, Y. W. & Fan, H. F. (1987). *Acta Cryst.* A**43**, 820–824.

Janssen, T., Janner, A., Looijenga-Vos, A. & Wolff, P. M. de (1992). *International Tables for Crystallography.* Volume C, edited by A. J. C. Wilson. Dordrecht: Kluwer Academic.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1992). *Solid State Commun.* **82**, 345–349.

Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1993). *Acta Cryst.* A**49**, 709–721.

Lam, E. J. W., Beurskens, P. T. & Smaalen, S. van (1994). *Acta Cryst.* A**50**. In press.

Yamada, N. & Ikeda, T. (1984). *J. Phys. Soc. Jap.* **53**, 2555–2564.

6

Determination of the Incommensurately Modulated Structure of (Perylene)Co(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ by Direct Methods*

Abstract

For the organic conductor (perylene)Co(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$, where mnt is maleonitriledithiolate, the incommensurate displacive modulation is determined by using X-ray diffraction data for main reflections and first- and second-order satellites, collected at a temperature of 283 K. The lattice parameters of the unit cell of the average structure are: a = 6.5441(13) Å, b = 11.7173(15) Å, c = 16.4251(17) Å, α = 92.092(11)°, β = 95.343(16)°, γ = 94.67(2)° with V = 1248.6(3) Å^3 and Z = 2. The components of the modulation wave vector are given by: q_1 = 0.211(13), q_2 = −0.1374(5), q_3 = −0.368(2). The symmetry of the modulated structure is given by the (3+1)-dimensional superspace group $P\bar{1}(q_1, q_2, q_3)$. Direct methods were used to obtain a starting model for the modulation. The subsequent refinement converged to R = 0.126 for 2835 observed ($I/\sigma > 2.5$) reflections. Partial R factors are 0.111 for 1450 main reflections, 0.143 for 1188 first-order satellites and 0.263 for 197 second-order satellites. The modulation is described by sawtooth-shaped functions for the Co and S atoms and by rigid-body modulations, up to third-order harmonics, for the perylene units and parts of the mnt fragments. The largest amplitudes were found for the Co atom (0.77 Å) and the S atoms (0.48 to 0.63 Å) and were mainly directed along the **a** axis. The four equatorial Co–S distances are only slightly affected by the modulation but the two apical Co–S distances show large variations with distances ranging from 2.05 to 3.86 Å. These variations are out of phase. This causes the coordination of the Co atom to vary from a distorted octahedral coordination by six sulfur atoms to a region with five-fold coordination and *vice versa*. The valence of the Co atom, as calculated by the bond-valence method, varies between 2.92 and 3.57. The stacking of the Co(mnt)$_2$ units can be described by oligomeric packages of 4 or 5 dimerized Co(mnt)$_2$ units.

*Lam, E. J. W., Beurskens, P. T., Smits, J. M. M., Smaalen, S. van, Boer, J. L. de & Fan, H.-F. (1994). Submitted.

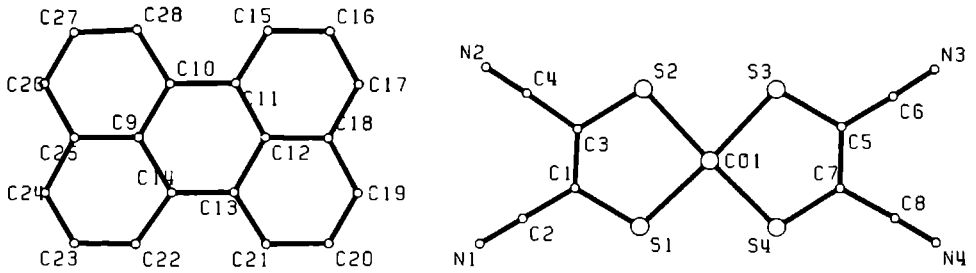


Figure 6.1. Geometry of the molecular units. (*a*) Perylene molecule (H atoms not shown). (*b*) $Co(mnt)_2$ unit.

6.1 Introduction

(Perylene)$Co(mnt)_2(CH_2Cl_2)_{0.5}$ (denoted PECO) belongs to a series of molecular conductors based on perylene (Figure 6.1*a*) and metal-bis(dithiolenes) of the type $M(mnt)_2$ (Figure 6.1*b*) with general formula $(perylene)_nM(mnt)_2$, where M is a metal atom, mnt is maleonitriledithiolate and $n = 1, 2$. The average structure of PECO at room temperature is triclinic, space group $P\bar{1}$ with 2 formula units in the unit cell (Gama *et al.*, 1992). The structure contains polymeric chains of $Co(mnt)_2$ units alternated by almost uniform stacks of perylene molecules along the **a** axis. The dichloromethane molecules are situated at centers of symmetry and are therefore disordered. Each Co atom appears to be octahedrally coordinated by S atoms. The four equatorial S atoms [*e.g.* atoms S(1–4), see Figure 6.2] and the Co atom all belong to the same $Co(mnt)_2$ unit but each apical S atom [*e.g.* atom S(1′) or atom S(4′), see Figure 6.2] is an equatorial S atom in a neighboring $Co(mnt)_2$ unit. Thus, each $Co(mnt)_2$ unit shares two Co–S bonds with each of the two neighboring units. As a result, stacks are formed of Co–S octahedrons sharing a single S_{apical}–$S_{equatorial}$ edge with each neighbor. The two S atoms along this common edge are related to one another by a center of symmetry. Differences in inter-$Co(mnt)_2$ contacts suggest that the polymeric chain of $Co(mnt)_2$ units can also be described as a chain of dimerized $Co(mnt)_2$ units (Gama *et al.*, 1992).

The present paper is concerned with the determination of the incommensurately modulated structure of PECO. A starting model for the refinement of the modulation was obtained from a multidimensional direct-methods procedure (Hao, Liu & Fan, 1987; Fu & Fan, 1994), where, for both main reflections and first-order satellites, normalized structure factors were used instead of common structure factors (Lam, Beurskens & van Smaalen,

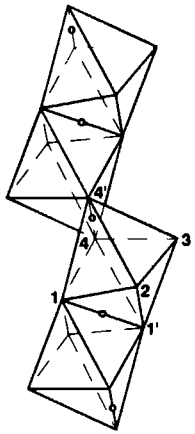


Figure 6.2. Part of the chain of Co–S octahedrons along the **a** axis. The two octahedrons at the bottom of the figure form one dimer and the two octahedrons at the top of the figure form the other dimer. The viewing direction is along $\mathbf{c}^*$ on the $(\mathbf{a}, \mathbf{b})$ plane. Small circles represent centers of symmetry. Numbers n represent atoms S(n).

1992, 1993, 1994). The modulation is found to be large (amplitudes of 0.77 Å for cobalt and of 0.48 to 0.63 Å for sulphur) and is related to a mixed valence state of the Co atoms (valence fluctuations ranging from 2.92 to 3.57). Therefore, not all Co atoms are octahedrally coordinated as suggested by the average structure.

6.2 X-ray diffraction experiment

The diffraction pattern of crystals with an incommensurate one-dimensional modulation is characterized by the presence of strong main reflections at the nodes of the reciprocal lattice $\{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*\}$ of the average structure, accompanied by satellite reflections that are usually weaker (Janssen, Janner, Looijenga-Vos & de Wolff, 1992; van Smaalen, 1994; and references therein). The complete diffraction pattern can be indexed by four integers $(hklm)$, according to $\mathbf{S} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^* + m\,\mathbf{q}$, where $\mathbf{q} = q_1\,\mathbf{a}^* + q_2\,\mathbf{b}^* + q_3\,\mathbf{c}^*$ is the modulation wave vector.

The average structure, given by the main reflections ($m = 0$), was determined by Gama *et al.* (1992), using 6039 main reflections of which 3948 were observed.† On the

†Refinement of the average structure, using main reflections only, allowed the positioning of a disordered C atom (denoted C29 with occupancy factor 1/2), which was not given in the list of coordinates by Gama *et al.* (1992).

same crystal, hereafter called crystal 1, intensities of first-order satellites ($|m| = 1$) were also measured, in a hemisphere up to $\theta = 20°$ for Mo-Kα radiation. A total of 4773 unique satellite reflections were obtained of which 1640 reflections were denoted as observed ($I/\sigma > 2.5$). Lattice parameters were reported as $a = 6.551(1)$ Å, $b = 11.732(2)$ Å, $c = 16.481(2)$ Å, $\alpha = 92.08(1)°$, $\beta = 95.30(1)°$ and $\gamma = 94.62(1)°$. The modulation wave vector was reported as $\mathbf{q} = (0.224, -0.132, -0.359)$. Crystal 1 appeared to be twinned, with the twinning matrix given by

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\mathrm{II}} = \begin{pmatrix} -1.004 & -0.005 & -0.001 \\ 0.310 & 0.310 & 0.695 \\ 0.319 & 1.314 & -0.306 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\mathrm{I}},$$

where the subscripts I and II denote the two domains. It follows that the domains have a common **a** axis, but no definite relationship (twinning law) could be found in other directions, either in direct space or in reciprocal space. Because the unit cell is triclinic, overlap between reflections of the two domains will only occur at special points. Analysis of the final refinement did not show any systematic influence of the twinning. Therefore, the intensities of domain I were used in the refinements without any correction.

Motivated by the relatively large R factors for the main reflections after the final refinement and the unsatisfactory geometry of the model (Section 6.4), a second crystal was selected for data collection (crystal 2). This crystal was four times smaller than crystal 1, making it more difficult to measure the weak satellites. On the other hand, crystal 2 was not twinned, thus excluding contamination of the intensities by a second domain. Nevertheless, the fit to the main reflections did not improve and the relatively high R factors must be ascribed to intrinsic effects.

For crystal 2, X-ray diffraction experiments were performed at a temperature of 283 K on an Enraf-Nonius CAD–4F diffractometer employing Mo-Kα radiation ($\lambda = 0.71073$ Å). Dimensions of the unit cell of the average structure were determined from a least-squares treatment of the setting angles of 25 main reflections with $6° < \theta < 17°$. Similarly, the components of the modulation wave vector were determined from 8 first-order satellites with $7° < \theta < 16°$. As satellite reflections were very weak and required about 10 minutes measuring time each, it was decided to measure only those reflections which could be expected to be 'observable'. All main reflections and first-order satellites measured on crystal 1, which satisfied the condition $I/\sigma > 1.5$, were measured for crystal 2. Also, 3000 second-order satellites having the largest calculated intensities were measured: these intensities were calculated using the parameters of the model which was refined with the data measured for crystal 1, where first- and second-order harmonics were used to describe

Table 6.1. Summary of X-ray diffraction data for crystal 2

Crystal			
Color, dimensions (mm^3)	black, 0 05 × 0 16 × 0 42		
μ[Mo-Kα] (cm^{-1})	11 429		
D_{calc} (gr cm^{-3})	1 687		
Intensity measurements			
Reflection order ($\|m\|$)	0	1	2
Scan method	ω	ω	ω
Scan width (°)	1 95	1 95	1 95
Max scan time (s)	300	300	600
θ_{max} (°)	29	21	29
h range	0, 8	0, 6	0, 9
k range	−15, 15	−11, 11	−15, 15
l range	−21, 21	−15, 15	−20, 20
Intensity control reflections	1, −1, −6, 0	1, −1, −6, 0	1, −1, −6, 0
	1, 4, −2, 0	1, 4, −2, 0	1, 4, −2, 0
	−2, 1, −2, 0	−2, 1, −2, 0	−2, 1, −2, 0
Monitoring interval (hours)	1	1	2
Drift correction (%)	2 1	3 3	7 5
Min /max absorption correction factors	0 773/1 226	0 774/1 226	0 773/1 224
No of unique reflections	2677	2107	3000
No of unique reflections with $I/\sigma > 2.5$	1450	1188	197
Average structure			
a, b, c (Å)	6 5441(13), 11 7173(14), 16 4251(17)		
α, β, γ (°)	92 092(11), 95 343(16), 94 67(2)		
Z, V (Å^3)	2, 1248 6(3)		
Space group	$P\bar{1}$ (No 2)		
Modulated structure			
q_1, q_2, q_3	0 211(13), −0 1374(5), −0 368(2)		
Superspace group	$P\bar{1}(q_1, q_2, q_3)$ (No 2)		

the modulations Reflections within a hemisphere were measured Crystal and instrumental stability were checked throughout the data collection by monitoring the intensities of three main reflections Variations in these intensities were corrected by a smoothed curve On all reflections, profile analysis was performed using a local program which combines the methods of Lehman & Larsen (1974) and Grant & Gabe (1978) Reflection profiles appeared to be elongated along the **a*** direction, which caused a relatively large standard deviation in this component of the modulation wave vector An *ab initio* empirical absorption correction was applied using the local program *EMPABS*, based on the method of North, Philips & Mathews (1968) After Lorentz and polarization corrections, the data were reduced to $|F_{obs}|$ values (see Table 6 1 for details)

Comparison of observed structure factors for both crystals led to conventional disagreement factors $R = 0.133$, $R = 0.124$ and $R = 0.150$ for, respectively, all reflections, main reflections and first-order satellites

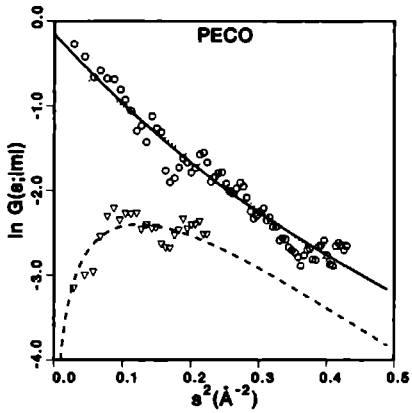


Figure 6.3. Natural logarithm of the seminormalized average intensities $G(s;|m|)$ as a function of s^2, where $s = (\sin\theta)/\lambda$. Circles (main reflections) and triangles (first-order satellites) represent experimental values obtained as $G(s;|m|) = \langle I/\sum_\mu f_\mu(s)\rangle_{s,|m|}$, where the summation extends over all atoms μ in the unit cell of the average structure. The average $\langle\cdots\rangle_{s,|m|}$ is taken in intervals of s at constant $|m|$. The dotted line represents a conventional Wilson plot (K = 1.217 and B = 3.05 Å^2) against main reflections only. The solid and dashed lines describe the fits against main reflections and first-order satellites, respectively, and were obtained in a single fit procedure (Lam, Beurskens & van Smaalen, 1992, 1994).

6.3 Direct-methods solution

Data measured on crystal 1 were used to determine the phases of the satellite reflections by a direct-methods procedure. Estimates of the scale factor (K), the overall isotropic temperature parameter (B) and the overall modulation parameter (U_1) were obtained by a statistical procedure (Lam, Beurskens & van Smaalen, 1992, 1994). With only main reflections and first-order satellites available, the modulation parameter (U_1) represents a weighted average, over all atoms, of the first-order harmonic components of the modulation functions. Because lack of stoichiometry is unlikely to occur in this structure, only displacive modulations are considered here. The average intensities are plotted in Figure 6.3. The fitted parameters, K = 1.081, B = 1.96 Å^2 and U_1 = 0.421 Å, were used for the calculation of normalized structure factors (Lam, Beurskens & van Smaalen, 1993).

The phases of the main reflections calculated from the known average structure can be used as good approximations for the phases of the main reflections of the modulated structure. It has been shown that these phases, together with the measured intensities of the main reflections and satellites, can be used to determine the phases of the satellites

(Hao, Liu & Fan, 1987). This method is employed in the computer program *DIMS* (Fu & Fan, 1994).

Initially, structure factors (F) were used in a default run of *DIMS*. The 1000 strongest main reflections with calculated phases were kept fixed in the procedure. Starting phases for the 1000 strongest satellite reflections were assigned at random, creating 20 different phase sets. These phases were refined in ten cycles by use of the four-dimensional Sayre equation. Not more than 300 triplet relations were allowed to contribute to a single satellite phase. The best set of satellite phases was selected with the default combined figure-of-merit. It appeared that all 20 refined phase sets were nearly identical.

In a restart of the direct-methods procedure, normalized structure factors (E) were used. All reflections having $|E| \geq 1.25$ (925 main reflections and 642 first-order satellites) were input to the program *DIMS*, in an otherwise default run (as above). All 20 solutions generated by *DIMS* were identical and contained 46 satellites with incorrect phases. A similar default run using the same number of strongest $|F|$ values gave 20 nearly identical phase sets with the best solution having 54 incorrect phases. This is in agreement with de Gelder *et al.* (1994), who found that the use of $|E|$ values generally results in a slightly better convergence of the refinement by the Sayre equation.

Four-dimensional electron-density maps were calculated from the phased structure factors (F) by use of the program *FOURIER* (Petříček, 1993). These maps clearly reveal the displacements of the Co and S atoms: large displacements along the **a** axis and much smaller displacements along the **b** and **c** axes. The displacements of the Co and S atoms in one Co(mnt)$_2$ unit are approximately in phase. Electron-density maps for atoms Co and S(1) are given in Figures 6.4(a) and (b), respectively. The following estimates were obtained for the first-order harmonics of the modulation functions of the Co and S atoms:

$$\begin{aligned} \text{Co}, \quad & a_{1,x}^{\mu,s} = -0.07; \\ \text{S(1–4)}, \quad & a_{1,x}^{\mu,s} = -0.05. \end{aligned}$$

Initial values for the other amplitudes of these atoms are taken as zero [see (6.1) for definition]. Note that these large displacements along the **a** axis could be inferred also from the large values of the temperature parameter U_{11} of these atoms in the average structure (Gama *et al.*, 1992), but their numerical values and their relative phases only follow from the direct-methods procedure.

From the electron-density maps, it can be seen that the displacements of the Co atom and the atoms S(1–4) more look like 'sawtooth' functions instead of the simple sine waves assumed above. This implies that higher-order harmonics have important contributions to the atomic displacements, as was confirmed by further analysis.

6.4 Refinement of the modulated structure

A model for the incommensurately modulated structure of PECO can be presented by specifying for each atom its average position, occupancy factor, temperature parameters and displacive modulation functions. A full-matrix least-squares refinement on $|F_{obs}|$ values of the structural parameters was done with the program *JANA* (Petříček & Coppens, 1988; Petříček, 1993), minimizing the function wR,

$$wR = \left[\frac{\sum w(|F_{obs}| - |F_{calc}|)^2}{\sum w\,|F_{obs}|^2}\right]^{1/2},$$

using the weighting scheme $w = (\sigma^2 + 0.02\,|F_{obs}|^2)^{-1}$.

The modulation functions

The position of an atom μ in an incommensurately modulated structure is given by $\mathbf{r}(\mu, \mathbf{L}_\mu) = \mathbf{r}_0^\mu + \mathbf{L}_\mu + \mathbf{u}^\mu$, where $\mathbf{r}_0^\mu = (x_0^\mu, y_0^\mu, z_0^\mu)$ is the average position of the atom relative to the origin in the unit cell of the average structure, $\mathbf{L}_\mu$ is a lattice vector of the average structure and $\mathbf{u}^\mu = (u_x^\mu, u_y^\mu, u_z^\mu)$ describes the atomic displacement functions. The latter are periodic functions, with period 1, of the four-dimensional coordinate $\bar{x}_4^\mu = \mathbf{q}\cdot(\mathbf{r}_0^\mu + \mathbf{L}_\mu) + t$, where t is the internal parameter (de Wolff, 1974). With the program *JANA*, the following displacive modulation functions can be used. [Note, all vectors are described with respect to the basis (**a**, **b**, **c**) of the average structure with the subscript $i = x, y, z$ denoting the various components, respectively.]

(1) For individual atoms, the most general form of a displacement function is given by a truncated Fourier series:

$$u_i^\mu(\bar{x}_4^\mu) = \sum_n \left[a_{n,i}^{\mu,s} \sin(2\pi n \bar{x}_4^\mu) + a_{n,i}^{\mu,c} \cos(2\pi n \bar{x}_4^\mu)\right], \tag{6.1}$$

where $a_{n,i}^{\mu,s}$ and $a_{n,i}^{\mu,c}$ are the amplitudes of the sine and cosine part, respectively, of the nth-order harmonic component and the summation extends over all harmonics with $n \geq 1$.

(2) Displacements of individual atoms can also be described by 'sawtooth' functions:

$$u_i^\mu(\bar{x}_4^\mu) = \frac{2u_{0,i}^\mu}{\Delta_\mu}(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu), \tag{6.2}$$

where $u_{0,i}^\mu$, $\bar{x}_{4,0}^\mu$ and Δ_μ are, respectively, the amplitude, the center and the width of the sawtooth function. This definition [(6.2)] applies within the interval $\bar{x}_{4,0}^\mu - \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu + \Delta_\mu/2$. The modulation function is defined as periodic, *i.e.* $u_i^\mu(\bar{x}_4^\mu + 1) = u_i^\mu(\bar{x}_4^\mu)$,

and is discontinuous at the interval boundaries. For $\Delta_\mu \neq 1$, the sawtooth function leads to occupancy factor modulation (Petříček, Gao, Lee & Coppens, 1990).

(3) The atomic displacement can also be described by a 'triangle' function, *i.e.* a combination of two sawtooth functions:

$$u_i^\mu(\bar{x}_4^\mu) = \begin{cases} \dfrac{2u_{0,i}^\mu}{\Delta_\mu}(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu) & (\bar{x}_{4,0}^\mu - \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu + \Delta_\mu/2) \\ \dfrac{-2u_{0,i}^\mu}{1-\Delta_\mu}(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu - 1/2) & (\bar{x}_{4,0}^\mu + \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu - \Delta_\mu/2 + 1), \end{cases} \tag{6.3}$$

again with a periodic continuation beyond the indicated intervals. In program *JANA*, this type of modulation can be mimicked by a substitutional modulation on two atoms (μ and ν), both of the same type and both having the same average position (which implies $\bar{x}_4^\mu = \bar{x}_4^\nu$), occupancy factor and thermal parameters. The displacement of the first atom (μ) is described by a sawtooth function [(6.2)], with parameters $u_{0,i}^\mu$, $\bar{x}_{4,0}^\mu$ and Δ_μ ($0 < \Delta_\mu < 1$). The displacement of the second atom (ν) is also described by a sawtooth function [(6.2)], but with parameters $u_{0,i}^\nu$, $\bar{x}_{4,0}^\nu$ and Δ_ν ($0 < \Delta_\nu < 1$) that are related to the modulation parameters of the first atom as:

$$u_{0,i}^\nu = -u_{0,i}^\mu, \quad \bar{x}_{4,0}^\nu = \bar{x}_{4,0}^\mu + 1/2, \quad \Delta_\nu = 1 - \Delta_\mu. \tag{6.4}$$

Note that, in contrast to the sawtooth function [(6.2)], with the triangle function [(6.3)], the occupancy factor of the combined atom, as a function of $\bar{x}_4^\mu$, is always equal to 1. As a result, no occupancy-factor modulation exists for the combined atom.

Rigid-body modulation

For atoms forming a specific group or molecule, the displacements of the individual atoms can be restricted in such a way that the geometry of the group is preserved ('rigid-body' modulation). The displacement of each atom is still described by (6.1), but with $\bar{x}_4^\mu$ replaced by $\bar{X}_4^k = \mathbf{q}\cdot\mathbf{R}^k + t$, where $\mathbf{R}^k$ is the phase-reference point of the kth rigid body, chosen as the center of mass of the rigid body. The atomic modulation parameters in (6.1) are expressed in terms of the translational and rotational displacements of the kth rigid-group:

$$a_{n,i}^{\mu,s} = [\mathbf{T}_n^{k,s} + \mathbf{W}_n^{k,s} \times (\mathbf{r}_0^\mu + \mathbf{L}_\mu - \mathbf{R}^k)]_i \tag{6.5}$$

and

$$a_{n,i}^{\mu,c} = [\mathbf{T}_n^{k,c} + \mathbf{W}_n^{k,c} \times (\mathbf{r}_0^\mu + \mathbf{L}_\mu - \mathbf{R}^k)]_i \tag{6.6}$$

Here, $\mathbf{T}_n^{k,s} = (t_{n,x}^{k,s}, t_{n,y}^{k,s}, t_{n,z}^{k,s})$ and $\mathbf{T}_n^{k,c} = (t_{n,x}^{k,c}, t_{n,y}^{k,c}, t_{n,z}^{k,c})$ represent, respectively, the sine and the cosine parts of the nth-order harmonic components of the translation of the rigid body. Similarly, the rotation of the rigid body, around the center of mass $\mathbf{R}^k$, is given by $\mathbf{W}_n^{k,s} = (w_{n,x}^{k,s}, w_{n,y}^{k,s}, w_{n,z}^{k,s})$ and $\mathbf{W}_n^{k,c} = (w_{n,x}^{k,c}, w_{n,y}^{k,c}, w_{n,z}^{k,c})$, respectively. Note that the rotational terms in (6.5) and (6.6) are rectilinear approximations to a true rotation and, therefore, are only valid with reasonable precision for rotations up to about 10°.

During structure refinement, the following groups were treated as rigid bodies. Groups NCN1 and NCN2, which are mnt-groups without the sulphur atoms and PERYLENE, *i.e.* the perylene molecule, with hydrogen atoms at calculated positions. All atoms in these groups were assigned displacements given by (6.1), with the amplitudes defined by (6.5) and (6.6). Further, for each group, a single overall anisotropic temperature tensor has been used for all atoms of the group, except for the H atoms of the perylene molecule for which an overall isotropic temperature factor has been used. No rigid-body constraints were imposed upon the average positions of the atoms of the groups.

Introduction of rigid bodies was necessary because there happened to be a large number of rigid chemical bonds in the mnt fragments and the perylene molecule, causing the thermal parameters of atoms connected by these bonds to be highly correlated. Further, there were not enough second- and higher-order satellites to determine unambiguously the modulation parameters of harmonics of order higher than 1; it is known that thermal vibration and displacive modulation are highly correlated (Lam, Beurskens & van Smaalen, 1994). The introduction of rigid bodies greatly reduces the number of parameters needed to describe the modulated structure. As a result, the standard deviations of the temperature parameters and the modulation parameters of harmonics of order higher than 1 were significantly reduced. However, a slight increase in R factors was observed.

Initial refinement on data from crystal 1

Refinement of the modulated structure started from the average structure (Gama *et al.*, 1992), with estimates for the modulations of the Co and S atoms obtained as described above. The anisotropic temperature parameters of these atoms in the average structure were reduced accordingly (Lam, Beurskens & van Smaalen, 1994). Initial values for the modulation parameters of the other atoms were taken as zero. The dichloromethane molecule was included in the refinement with no modulation for the disordered C(29) atom. During the initial refinements, average positions of all atoms were kept fixed and only the perylene molecule was treated as a rigid body.

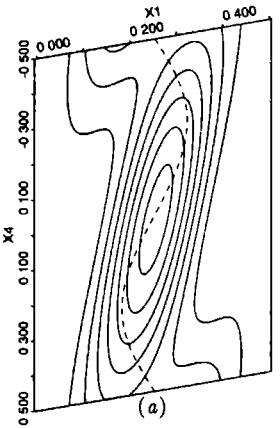
Refinement, allowing only first-order harmonics, converged smoothly to $R \simeq 0.17$ and

$R \simeq 0.32$ for main reflections and first-order satellites, respectively. With allowance for second-order harmonics, these R factors decreased to $R \simeq 0.13$ and $R \simeq 0.16$, respectively. The large decrease in the R factor for the satellites indicates that second-order harmonics, having atomic modulation amplitudes of 0.29 Å for the Co atom and of 0.46 to 0.49 Å for the S atoms, are indeed very important for the atomic displacements (see Section 6.3). The final refinement on crystal 1 was done using three rigid bodies: NCN1, NCN2 and PERYLENE. Temperature tensors and modulation parameters (harmonics with $n \leq 2$) of all individual atoms and of the three rigid bodies were included in the refinement. In addition, the average positions of all non-H atoms were also allowed to vary. The H atoms of perylene were refined riding on their parent C atoms with isotropic temperature parameters that were initially fixed at $U_{iso} = 0.06$ Å^2. R factors are 0.13 and 0.14 for main reflections and first-order satellites, respectively.

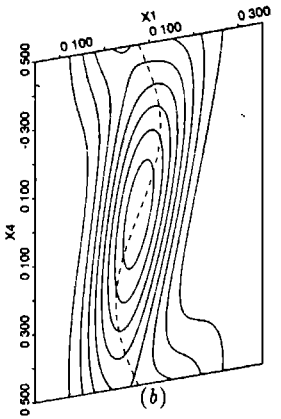
Unfortunately, the model at hand proved not to be very satisfactory. For the Co and S atoms, atomic displacements were not in good agreement with the electron-density maps of these atoms (Figures 6.4*c* and *d*). In addition, ranges of t values were found with too short Co–S distances, *e.g.* less than 1.8 Å. Also, because of the high R factors, the reflection data were suspected to suffer from overlap caused by twinning (Section 6.2), although tests could not provide convincing evidence for such influence. Further, because of the large modulation amplitudes of the first- and second-order harmonics of the displacements of the Co and S atoms, it was expected that second-order satellites might be strong. For these reasons, it was decided to measure new X-ray data on crystal 2.

Refinement on data from crystal 2

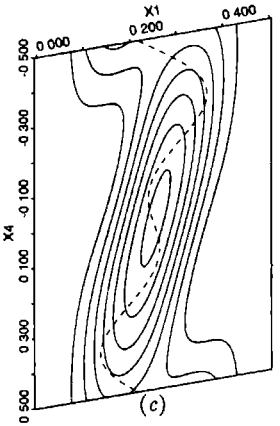
Refinement of the model, having only first- and second-order harmonics for the modulation functions of individual atoms and the rigid bodies, still resulted in relatively large R factors and in Co–S bonds that were too short. Alternatively, sawtooth functions [(6.2)] without occupancy factor modulation ($\Delta_\mu = 1$) were used to describe the displacements of the Co and S atoms. Considering the anharmonicity and the magnitudes of the displacements of the Co and S atoms, it is very likely that higher-order harmonics are also important for the modulations of the rigid bodies. Therefore, the modulation functions of the rigid bodies and the Cl atom were allowed to include all harmonics up to $n = 3$. Although the R factors were only slightly lower ($R = 0.11$, $R = 0.15$ and $R = 0.34$ for, respectively, main reflections, first- and second-order satellites), the sawtooth-shaped modulation function did give a much better description of the electron density and now only chemically reasonable values were found for the Co–S distances.


X1
0.000
0.200
0.400
X4
-0.500
-0.300
-0.100
0.100
0.300
0.500

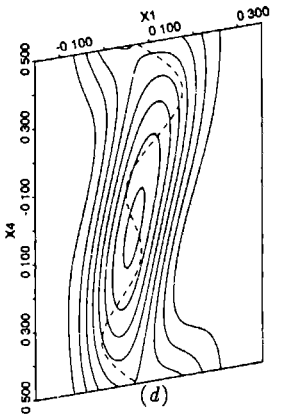
(a)


X1
0.100
0.100
0.300
X4
0.500
-0.300
0.100
0.100
0.300
0.500

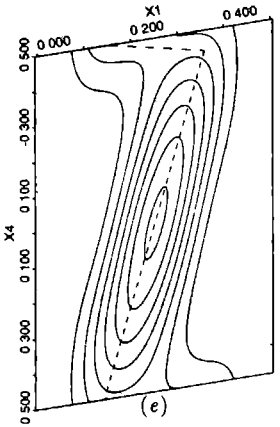
(b)


X1
0.000
0.200
0.400
X4
-0.500
-0.300
-0.100
0.100
0.300
0.500

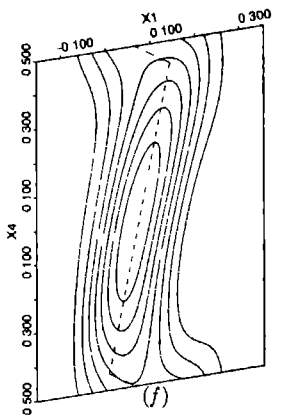
(c)


X1
-0.100
0.100
0.300
X4
0.500
0.300
-0.100
0.100
0.300
0.500

(d)


X1
0.000
0.200
0.400
X4
0.500
-0.300
0.100
0.100
0.300
0.500

(e)


X1
-0.100
0.100
0.300
X4
0.500
0.300
0.100
0.100
0.300
0.500

(f)

◁

Figure 6.4. Electron-density contours in the (x_1, x_4) plane, through the atoms Co and S(1), calculated from phased F_{obs} values. Contours of positive electron density are denoted by solid lines. Contours of zero and negative electron density are denoted by dotted lines. In addition, the x_1 components of the atomic modulation functions are indicated by dashed lines. Contour intervals are 8 electrons Å^{-3} for the Co atom and 4 electrons Å^{-3} for the S(1) atom. (*a*) Co atom. For main reflections, phases were calculated from the average structure (Gama *et al.*, 1992). For satellite reflections, phases were obtained from the direct-methods procedure. The modulation function (first-order harmonic) was calculated from the estimated modulation parameters. (*b*) S(1) atom. See (*a*) for explanation. (*c*) Co atom. Phases and modulation function (first- and second-order harmonics) were calculated using parameters obtained from the final refinement on crystal 1. (*d*) S(1) atom. See (*c*) for explanation. (*e*) Co atom. Phases and modulation function (sawtooth shaped) were calculated using parameters obtained from the final refinement on crystal 2. (*f*) S(1) atom. See (*e*) for explanation.

Further improvement of the fit (especially to the second-order satellites) was obtained by triangle functions [(6.3)] describing the modulations of the Co and S atoms (Figures 6.4*e* and *f*). The final R factor on a total of 330 structural parameters is 0.126 for 2835 observed ($I/\sigma \geq 2.5$) reflections. Partial R factors are 0.111, 0.143 and 0.263 for, respectively, 1450 main reflections, 1188 first-order satellites and 197 second-order satellites; corresponding wR values are 0.120, 0.185 and 0.279. Final values for the parameters describing average positions, thermal vibration and displacive modulations are given in Tables 6.2, 6.3 and 6.4, respectively.

6.5 Description of the modulated structure

Most of the Co atoms are octahedrally coordinated by S atoms. The four equatorial S atoms [S(1–4)] belong to the same Co(mnt)$_2$ unit and the two apical S atoms [S(1′) and S(4′)] belong to different neighboring Co(mnt)$_2$ units. Coordinates and modulation function of atom S(1′) are related to those of atom S(1) by a center of symmetry at $(0, 1/2, 0, 0)$ in four-dimensional space. Similarly, coordinates and modulation function of atom S(4′) are related to those of atom S(4) through a center of symmetry at $(1/2, 1/2, 0, 0)$.

Displacive modulations for the Co (amplitude 0.77 Å) and S atoms (amplitudes ranging from 0.48 to 0.63 Å) are mainly directed along the **a** axis. The displacements of the Co atom and its four equatorial S atoms are approximately in phase, causing the corresponding Co–S bonds to vary only slightly (between 2.14 and 2.34 Å) as a function of the internal parameter t (Table 6.5 and Figure 6.5). Because of the symmetry relation between atoms S(1′) and S(1) and, similarly, between atoms S(4′) and S(4), the displacement of the Co atom is approximately 180° out of phase with the displacements of the atoms S(1′) and

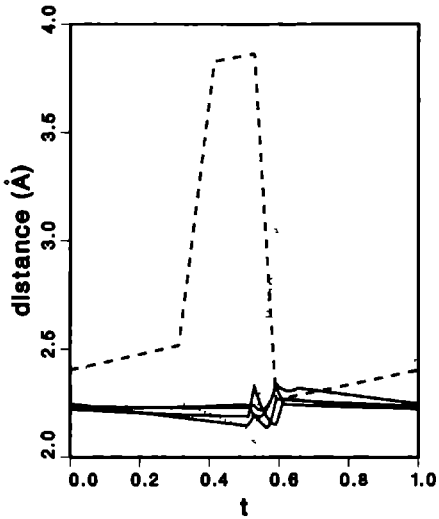


Figure 6.5. Distances between the Co atom and its coordinating S atoms as a function of the internal parameter t The continuous lines represent Co–S distances in the same $Co(mnt)_2$ unit, the dotted line represents the Co-S(1′) distances and the dashed line represents the Co S(4′) distances

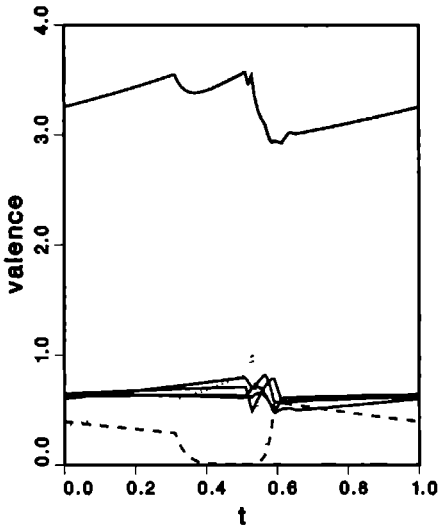


Figure 6.6. Valences for the Co–S bonds as a function of the internal parameter t The continuous lines in the lower half of the figure represent valences for Co–S bonds in the same $Co(mnt)_2$ unit, the dotted line represents the valence for the Co–S(1′) bond and the dashed line represents the valence for the Co–S(4′) bond The continuous line in the top half of this figure is the total valence of the Co atom

S(4′). As a result, the Co–S distances for the two apical S atoms show large variations, with distances ranging from 2.05 to 3.86 Å (Table 6.5 and Figure 6.5). For atom S(4′), there appears to be a region with relatively short Co–S distances (less than 2.5 Å) and a region where there is no bonding left (distances larger than 3.0 Å). The Co–S(1′) distance varies less than the Co–S(4′) distance, such that S(1′) is considered to be bonded to the Co atom for all values of t (despite the rather large distances around $t = 0.6$, see comments below). The picture emerges of a coordination of the Co atom which is either six-fold or five-fold. The ratio of the number of Co atoms in each type of coordination can be obtained from the width of the t interval corresponding to that type of coordination. For a distance of 3.0 Å, this width is equal to $\Delta t_{\rm exp} = 0.213$ (Figure 6.5). For chemical reasons (see below), it is inferred that this width is $\Delta t_{\rm th} = 0.211$, which means that 21.1% of all Co atoms are five-fold coordinated.

For incommensurate crystals, the bond-valence method due to Brown (1981) can be used to calculate valences of atoms as a function of the internal parameter t (van Smaalen, 1992). The valence of the Co atom as a function of t is given in Figure 6.6, together with the individual bond valences of its six coordinating S atoms [R_0 = 2.06 Å, from Brese & O'Keeffe (1991)]. The picture of a varying cobalt coordination is confirmed, as the bond valence of the Co–S(4′) bond is virtually zero for $0.40 < t < 0.55$, *i.e.* for these values of t the Co atom is only bonded to five S atoms. The valence of the Co atom varies between 2.92 and 3.57 and is indicative for a varying valence state of cobalt in this compound. The interpretation of relative values of the (bond-)valences, as has been done here, is certainly meaningful, but one should be cautious to use the absolute values because the employed bond-valence parameter was derived for inorganic salts and not for organometallic compounds.

For a chemical interpretation of the modulation in the bonding of the Co(mnt)$_2$ units, consider stepping along the **a** axis, *i.e.* along the chains of Co(mnt)$_2$ units, with stepsize $a = |\mathbf{a}|$. Each step is equivalent to a change $\Delta t_{\rm th} = q_1 = 0.211$ in the internal parameter t, corresponding to a periodicity of the modulation along the **a** axis of $4.74a$. Figure 6.5 then shows that after 4 to 5 steps along the **a** axis, the Co–S(4′) distance changes from bonding to nonbonding. The nonbonding state is restricted to this one step and changes to bonding again at the next step [the peak width $\Delta t_{\rm exp}$ in the Co–S(4′) distance plot corresponds very well to one step along the **a** axis]. Note that the Co(mnt)$_2$ units are always dimerized through S(1) and S(1′) (*i.e.* one dimer per average unit cell). These dimers form chains along the **a** axis connected through S(4) and S(4′). However, after 4 or 5 dimers, a gap in the chain occurs in the region where the Co–S(4′) bond becomes nonbonding. As a result the chains of Co(mnt)$_2$ units actually consist of oligomeric packages of 4 or 5

dimerized $Co(mnt)_2$ units and the Co atoms at the ends of each package only show five-fold coordination.‡

Furthermore, the chain of packages must make chemical sense: if after five dimers, the strain in a package (embedded in the perylene moiety of the structure) is released by one broken Co–S(4′) bond, the next package again is likely to consist of five dimers, and so on. But as the modulation is not commensurate, at some point a package may consist of only four dimers when the next Co–S(4′) bond is broken. The long-range order which exists in the structure makes it unlikely that some of the packages *by chance* consist of three or six dimers. If the chain of packages is considered to consist of N packages containing five dimers relative to one package containing four dimers, then the ratio x of the number of broken connections relative to the number of dimers can be written as $x = (N + 1)/(5N + 4) = \Delta t_{th} = 0.211$, from which it follows that $N = 2.84$. Thus, in first approximation, the chains consist of three packages containing five dimers alternated by one package containing four dimers, but at some point there are not three but just two packages containing five dimers, which prevents the modulation from being commensurate along the **a** axis.

One should realize that the description of the displacements of the Co and S atoms by triangle functions is an approximation to the true modulation of these atoms, introduced to restrict the number of variable parameters in the refinement to a manageable number. If higher-order harmonics could be refined properly, the variations in the Co–S distances are expected to become smoother. Therefore, the rather wild, but small, variations in the Co–S distances around $t = 0.55$ for atoms S(1–4) and S(1′) should not be taken too seriously. The same is true for the sharp maximum Co–S(1′) distance at $t = 0.6$. This also means that the differences between the minimum and maximum distances given in Table 6.5 should be narrowed.

Minimum values for the distances between cobalt and its coordinating sulphur atoms are thus in good agreement with the Co–S single-bond distance of 2.20 Å (Pauling, 1960). Also, the average distances (Table 6.5) between cobalt and its coordinating sulphur atoms are in good agreement with distances found for the same bonds in the average structure (Gama *et al.*, 1992).

‡Note. The packages of four or five dimerized $Co(mnt)_2$ units are the result of releasing the strain in the hypothetical chain of uninterrupted connected dimers. It is unlikely that a 'statistical' distribution of packages of four and five dimers is alternated by one package of one dimer ($\Delta t_{exp} > \Delta t_{th}$) or by one package of nine dimers ($\Delta t_{exp} < \Delta t_{th}$). Therefore, it is inferred that $\Delta t_{exp} = \Delta t_{th}$, which agrees very well within the experimental uncertainty.

Table 6.2. Fractional coordinates of the average atomic positions

These results are obtained from the final refinement against data collected from crystal 2 The standard deviations of the coordinates are given between parenthesis

Atom	x_0^μ	y_0^μ	z_0^μ	Atom	x_0^μ	y_0^μ	z_0^μ
Co	2509(9)	5577(3)	02520(19)	C(18)	218(4)	− 131(2)	4415(14)
S(1)	0756(13)	3892(5)	0376(3)	C(19)	198(4)	− 127(2)	3552(14)
S(2)	1739(14)	6177(5)	1480(3)	C(20)	203(4)	− 028(2)	3180(14)
S(3)	3913(14)	7359(5)	0155(4)	C(21)	228(4)	077(2)	3645(13)
S(4)	3820(14)	5006(5)	− 0875(3)	C(22)	279(4)	294(2)	4627(15)
C(1)	058(4)	387(2)	1432(12)	C(23)	305(4)	394(2)	5094(16)
C(2)	015(4)	283(2)	1791(13)	C(24)	331(4)	393(2)	5903(16)
C(3)	096(4)	487(2)	1885(12)	C(25)	320(4)	290(2)	6326(14)
C(4)	074(4)	495(2)	2745(12)	C(26)	350(4)	287(2)	7176(15)
N(1)	− 032(4)	1975(18)	2075(12)	C(27)	336(4)	187(2)	7558(15)
N(2)	064(3)	496(2)	3433(11)	C(28)	311(4)	081(2)	7117(13)
C(5)	453(4)	7356(19)	− 0837(13)	H(15)	264(6)	− 137(3)	674(2)
C(6)	513(4)	837(2)	− 1178(14)	H(16)	222(6)	− 314(3)	592(2)
C(7)	442(4)	6301(18)	− 1286(12)	H(17)	185(6)	− 308(3)	448(2)
C(8)	487(4)	634(2)	− 2128(13)	H(19)	180(6)	− 201(3)	3214(19)
N(3)	553(4)	9243(18)	− 1441(14)	H(20)	188(6)	− 029(3)	256(2)
N(4)	511(4)	6340(18)	− 2789(11)	H(21)	232(6)	151(3)	3369(18)
C(9)	295(4)	184(2)	5850(13)	H(22)	264(6)	295(3)	402(2)
C(10)	288(4)	079(2)	6243(13)	H(23)	309(6)	469(3)	482(2)
C(11)	264(4)	− 031(2)	5757(13)	H(24)	348(6)	468(3)	624(2)
C(12)	246(4)	− 027(2)	4899(13)	H(26)	373(6)	361(3)	751(2)
C(13)	248(4)	080(2)	4493(13)	H(27)	351(6)	188(3)	817(2)
C(14)	282(4)	184(2)	4959(13)	H(28)	307(6)	006(3)	7401(19)
C(15)	252(4)	− 136(2)	6126(15)	Cl	910(3)	9306(13)	0594(9)
C(16)	228(4)	− 239(2)	5650(14)	C(29)	046(14)	− 029(7)	− 024(5)
C(17)	206(4)	− 235(2)	4814(15)				

Table 6.3. Temperature parameters for individual atoms and rigid groups

These results are obtained from the final refinement against data collected from crystal 2 The standard deviations of the temperature parameters are given between parenthesis The correction to the atomic form factor because of thermal vibration is given by $\exp(-2\pi^2 \sum_{i,j=1}^{3} U_{ij} S_i S_j a_i^* a_j^*)$ for the anisotropic case and by $\exp[-8\pi^2 U(\sin\theta)^2/\lambda^2]$ for the isotropic case The isotropic temperature parameter for the H atoms of the perylene molecule is equal to $U = 0\ 05(2)$ Å^2 The temperature tensors of the groups NCN1 and NCN2 are not positive definite

Atom	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
Co	035(2)	0144(16)	0192(13)	− 0007(15)	0031(12)	0088(11)
S(1)	041(5)	029(4)	023(3)	001(4)	009(3)	006(3)
S(2)	046(4)	032(4)	026(3)	− 007(3)	007(3)	001(3)
S(3)	047(5)	023(3)	034(3)	− 005(3)	008(3)	005(3)
S(4)	036(4)	022(4)	029(3)	− 001(3)	− 003(3)	011(3)
Cl	22(2)	039(17)	11(2)	− 049(15)	050(16)	019(16)
C(29)	12(8)	08(6)	10(6)	02(6)	− 01(6)	− 07(5)

Group	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
NCN1	− 002(8)	008(12)	020(5)	005(8)	− 002(6)	008(7)
NCN2	020(9)	013(8)	016(8)	016(8)	014(7)	015(7)
PERYLENE	014(4)	035(4)	031(4)	003(3)	012(3)	013(3)

Table 6.4. Modulation parameters for individual atoms and rigid groups

These results are obtained from the final refinement against data collected from crystal 2. The standard deviations of the modulation parameters are given between parenthesis

Atom	$u^{\mu}_{0,x}$	$u^{\mu}_{0,y}$	$u^{\mu}_{0,z}$	$\bar{x}^{\mu}_{4,0}$	Δ_{μ}
Co	− 1082(9)	0201(5)	− 0094(3)	028(3)	938(12)
S(1)	− 069(2)	0113(12)	− 0008(7)	009(6)	89(4)
S(2)	− 072(2)	0159(12)	− 0040(7)	− 062(6)	95(4)
S(3)	− 091(2)	0083(11)	− 0093(8)	058(5)	86(3)
S(4)	− 096(2)	0035(11)	− 0004(7)	107(5)	90(3)

Atom	n	$a^{\mu,s}_{n,x}$	$a^{\mu,s}_{n,y}$	$a^{\mu,s}_{n,z}$	$a^{\mu,c}_{n,x}$	$a^{\mu,c}_{n,y}$	$a^{\mu,c}_{n,z}$
Cl	1	− 029(4)	− 0242(19)	− 0004(14)	006(4)	014(2)	0044(15)
	2	024(7)	− 014(4)	002(2)	033(6)	− 014(3)	006(2)
	3	004(10)	022(4)	011(4)	− 007(11)	001(5)	− 016(4)

Group	n	$t^{k,s}_{n,x}$	$t^{k,s}_{n,y}$	$t^{k,s}_{n,z}$	$t^{k,c}_{n,x}$	$t^{k,c}_{n,y}$	$t^{k,c}_{n,z}$
NCN1	1	− 022(2)	0070(15)	− 0001(8)	− 010(2)	0127(16)	− 0009(10)
	2	020(4)	010(3)	0011(16)	015(4)	002(3)	− 0015(14)
	3	− 012(5)	− 011(4)	− 003(4)	− 021(6)	016(4)	003(2)
NCN2	1	− 035(2)	0032(16)	− 0077(10)	009(2)	0042(15)	− 0018(9)
	2	− 012(4)	− 004(3)	0013(15)	001(4)	− 011(3)	0053(16)
	3	− 006(8)	000(4)	− 002(3)	024(6)	− 006(3)	− 010(2)
PERYLENE	1	− 0068(10)	0056(8)	− 0052(5)	0021(14)	0022(9)	− 0009(5)
	2	− 003(2)	0005(18)	0060(10)	− 001(3)	− 002(2)	0012(11)
	3	006(5)	− 004(2)	− 0038(13)	008(4)	− 002(3)	− 0009(18)

Group	n	$w^{k,s}_{n,x}$	$w^{k,s}_{n,y}$	$w^{k,s}_{n,z}$	$w^{k,c}_{n,x}$	$w^{k,c}_{n,y}$	$w^{k,c}_{n,z}$
NCN1	1	0032(14)	0029(12)	0013(7)	− 0011(16)	0075(14)	− 0001(8)
	2	− 001(3)	006(2)	− 0005(12)	000(2)	− 0045(19)	− 0021(11)
	3	004(4)	− 001(3)	− 0059(14)	− 006(3)	006(2)	0017(17)
NCN2	1	− 0008(16)	0008(13)	0009(8)	0079(15)	0081(14)	0021(8)
	2	− 010(2)	− 002(2)	− 0009(11)	− 001(2)	− 009(2)	− 0014(13)
	3	− 003(4)	007(4)	003(2)	− 007(2)	− 002(3)	− 0044(13)
PERYLENE	1	− 0015(6)	− 0014(4)	− 0004(3)	0007(5)	0028(3)	− 0004(2)
	2	0073(8)	0008(8)	0026(5)	− 0019(11)	0013(5)	0007(4)
	3	0059(11)	− 0011(13)	0002(6)	0022(17)	0050(10)	0012(7)

Table 6.5. Minimum, average and maximum Co–S distances

Bond	Minimum distance (Å)	Average distance (Å)	Maximum distance (Å)	Distance (Å) by Gama *et al* (1992)
Co–S(1)	2 22	2 23	2 33	2 23
Co–S(2)	2 14	2 23	2 27	2 23
Co–S(3)	2 15	2 23	2 34	2 23
Co–S(4)	2 15	2 22	2 33	2 23
Co–S(1′)	2 05	2 42	3 06	2 44
Co–S(4′)	2 27	2 68	3 86	2 62

Acknowledgements

The authors thank Dr M Almeida (Laboratório Nacional de Engenharia e Tecnologia Industrial) for making available the crystals, Dr V Petříček (Academy of Sciences of the Czech Republic) for making available the Computing System *JANA*93 and Professor A Janner (University of Nijmegen) for many stimulating discussions Part of this work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO)

References

Brese, N E. & O'Keeffe, M. (1991) *Acta Cryst* B**47**, 192–197

Brown, I D. (1981) *Structure and Bonding in Crystals*, Vol 2, edited by M O'Keeffe & A Navrotsky, pp 1–30 New York Academic Press

Fu, Z.-Q. & Fan, H -F (1994) *J Appl Cryst* **27**, 124 127

Gama, V., Henriques, R. T., Bonfait, G., Almeida, M., Meetsma, A , Smaalen, S. van & Boer, J L. de (1992) *J Am Chem Soc* **114**, 1986 1989

Gelder, R. de, Lam, E. J. W , Israël, R , Beurskens, P T., Smaalen, S. van, Fu, Z.-Q. & Fan, H -F (1994) In preparation

Grant, D. F & Gabe, E J. (1978) *J Appl Cryst* **11**, 114–120

Hao, Q., Liu, Y -W & Fan, H -F. (1987) *Acta Cryst* A**43**, 820–824

Janssen, T , Janner, A , Looijenga-Vos, A & Wolff, P M de (1992) *International Tables for Crystallography* Volume C, edited by A J C Wilson Dordrecht Kluwer Academic

Lam, E. J. W., Beurskens, P. T. & van Smaalen, S (1992) *Solid State Comm* **82**, 345–349

LAM, E. J. W., BEURSKENS, P. T. & VAN SMAALEN, S. (1993). *Acta Cryst.* A**49**, 709–721.

LAM, E. J. W., BEURSKENS, P. T. & VAN SMAALEN, S. (1994). *Acta Cryst.* A**50**. In press.

LEHMAN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

NORTH, A. C. T., PHILIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd edition, pp. 255–256. New York: Cornell University Press.

PETŘÍČEK, V. (1993). *The Computing System JANA*93. Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 16200 Praha 6, Czech Republic.

PETŘÍČEK, V. & COPPENS, P. (1988). *Acta Cryst.* A**44**, 235–239.

PETŘÍČEK, V., GAO, Y., LEE, P. & COPPENS, P. (1990). *Phys. Rev. B* **42**, 387–392.

SMAALEN, S. VAN (1992). *Acta Cryst.* A**48**, 408–410.

SMAALEN, S. VAN (1994). *Crystallography Reviews.* In press.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.

7

Direct Methods for Incommensurate Intergrowth Compounds. I. Determination of the Modulation*

Abstract

A direct method is proposed for the determination of the modulation in incommensurate intergrowth compounds. The method is based on a new type of Sayre equation that relates the phase of a satellite reflection to the sum of structure-factor products of pairs of main reflections. Phases of satellite reflections are thus uniquely determined by the phases of main reflections. This reflects the fact that the modulation in intergrowth structures is the result of the interaction of all of the subsystems that form the basic structure. Test calculations were done with experimental data of two known composite structures of the inorganic misfit layer compounds $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. The results showed that the method is accurate and efficient and is fully independent of any preliminary assumption of the model of modulation.

*Published as: Fan, F.-H., Smaalen, S. van, Lam, E. J. W. & Beurskens, P. T. (1993). *Acta Crystallographyca*, A**49**, 704–708.

7.1 Introduction

Incommensurate intergrowth compounds can be considered as coherent combinations of two or more modulated structures (Janner & Janssen, 1980; van Smaalen, 1992). Each of the structures (subsystems) is characterized by a unit cell and a set of modulation wave vectors. The diffraction pattern has main reflections at the nodes of each of the reciprocal lattices of the subsystems and has satellites at positions defined by the modulation wave vectors. Usually, two subsystems have a common reciprocal-lattice plane, thus providing only a single incommensurate direction. The coherent intergrowth means that the basic periodicities of one subsystem provide the modulation periods in the other subsystem. Composite structures or incommensurate intergrowth compounds differ from ordinary incommensurately modulated structures in that they do not have three-dimensional periodic basic structures. The basic structure of an incommensurate intergrowth compound is already a four- or higher-dimensional periodic structure.

Multidimensional direct methods (Hao, Liu & Fan, 1987; Xiang, Fan, Wu, Li & Pan, 1990; Mo, Cheng, Fan, Li, Sha, Zheng, Li & Zhao, 1992) have been proposed and successfully used for the determination of incommensurately modulated structures having three-dimensional basic structures. In this paper, the method is extended to incommensurately modulated structures having four- or higher-dimensional periodic basic structures. In this case, a new type of Sayre phase relation is found, which relates the phase of a satellite reflection to the sum of structure-factor products of pairs of main reflections. This makes it possible to compute the phases of the satellite reflections from the structure factors of the main reflections and, thus, to determine the modulation. The method is illustrated by its application to the known structures of the inorganic misfit layer compounds $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$.

7.2 The method

According to the multidimensional Sayre equation (Hao, Liu & Fan, 1987), for an incommensurately modulated structure we have the following phase relation:

$$\varphi[F(\mathbf{H})] = \varphi\left[\sum_{\mathbf{H}'} F(\mathbf{H}')F(\mathbf{H}-\mathbf{H}')\right], \tag{7.1}$$

where $\varphi[F(\mathbf{H})]$ denotes the phase of $F(\mathbf{H})$ and $F(\mathbf{H})$ is the structure factor with multidimensional reciprocal-lattice vector $\mathbf{H}$. The summation on the right-hand side of (7.1) can

be split into three parts, *i.e.*

$$\varphi[F(\mathbf{H})] = \varphi\left[\sum_{\mathbf{H}'} F_m(\mathbf{H}')F_m(\mathbf{H}-\mathbf{H}') + \sum_{\mathbf{H}'} F_m(\mathbf{H}')F_s(\mathbf{H}-\mathbf{H}') + \sum_{\mathbf{H}'} F_s(\mathbf{H}')F_s(\mathbf{H}-\mathbf{H}')\right]. \quad (7.2)$$

Here, the subscript m is used for main reflections while the subscript s is used for satellites. Because the intensities of satellites are on average much weaker than those of main reflections, the last summation on the right-hand side of (7.2) is negligible in comparison with the second, while the last two summations on the right-hand side of (7.2) are negligible in comparison with the first. Now, if $F(\mathbf{H})$ on the left-hand side of (7.2) represents the structure factor of a main reflection, we have, to a first approximation,

$$\varphi[F_m(\mathbf{H})] \simeq \varphi\left[\sum_{\mathbf{H}'} F_m(\mathbf{H}')F_m(\mathbf{H}-\mathbf{H}')\right]. \quad (7.3)$$

This implies that it is possible to solve the basic structure in multidimensional space using only main reflections. On the other hand, if $F(\mathbf{H})$ on the left-hand side of (7.2) represents the structure factor of a satellite, we have

$$\varphi[F_s(\mathbf{H})] \simeq \varphi\left[\sum_{\mathbf{H}'} F_m(\mathbf{H}')F_m(\mathbf{H}-\mathbf{H}') + \sum_{\mathbf{H}'} F_m(\mathbf{H}')F_s(\mathbf{H}-\mathbf{H}')\right]. \quad (7.4)$$

For a conventional incommensurately modulated structure, the first summation on the right-hand side of (7.4) will be equal to zero because the sum of two lattice vectors, $\mathbf{H}'$ and $\mathbf{H}-\mathbf{H}'$, belonging to the same three-dimensional reciprocal lattice can never produce a point outside that lattice (satellite). Therefore, (7.4) reduces to

$$\varphi[F_s(\mathbf{H})] = \varphi\left[\sum_{\mathbf{H}'} F_m(\mathbf{H}')F_s(\mathbf{H}-\mathbf{H}')\right]. \quad (7.5)$$

However, for an incommensurate intergrowth compound having a four- or higher-dimensional basic structure, the first summation on the right-hand side of (7.4) will not vanish. Hence, we have instead of (7.5) the following phase relation:

$$\varphi[F_s(\mathbf{H})] = \varphi\left[\sum_{\mathbf{H}'} F_m(\mathbf{H}')F_m(\mathbf{H}-\mathbf{H}')\right], \quad (7.6)$$

where $\mathbf{H}'$ and $\mathbf{H}-\mathbf{H}'$ are main reflections of two different subsystems.

Equations (7.5) and (7.6) are two different types of phase relation. The former has already been used successfully in solving conventional incommensurately modulated structures (Xiang *et al.*, 1990; Mo *et al.*, 1992), while the latter can be used for deriving phases of satellite reflections of a composite structure provided its basic structure is known. In terms of structure analysis, (7.6) includes more information than (7.5) does. Equation (7.5) just tells us how the phases of satellite reflections are related through the main reflections, while (7.6) can tell us how the phases of satellite reflections are uniquely determined by the main reflections. This is not surprising when we consider the fact that the incommensurate modulation in a composite structure is the result of the interaction of different subsystem structures, which together form the basic structure. Equations (7.3) and (7.6) provide the basis of a two-step procedure for solving composite structures:

(1) The basic structure is determined from the main reflections only;

(2) The incommensurate modulation is determined by the derivation of phases of satellite reflections from the known phases of main reflections.

7.3 Test and results

(1) *Test data*

$(LaS)_{1.14}NbS_2$ consists of two subsystems (Figure 7.1). Both are orthorhombic, with superspace groups $Fm2m(\alpha,0,0)\bar{1}\bar{1}s$ for NbS_2 and $Cm2a(\alpha^{-1},0,1/2)\bar{1}\bar{1}1$ for LaS. The basic structure can be described as the alternate stacking of two types of layers (Wiegers *et al.*, 1990). The first subsystem comprises the three-atom-thick NbS_2 layers. Their structure is equivalent to that of a single layer in pure NbS_2. The LaS layers form the second subsystem. They can be regarded as two-atom-thick (100) slices of a rock-salt-type structure. Perpendicular to the layers, the two subsystems have the same periodicity $\mathbf{c}^*$. Within the layers, the reciprocal axis $\mathbf{b}^*$ is common to the two subsystems (Figure 7.1*a*), while the two $\mathbf{a}^*$ axes are different, thus providing the incommensurateness (Figure 7.1*b*). The modulation was shown to be relatively small, with displacement amplitudes of the order of 0.1 Å (van Smaalen, 1991). The reciprocal lattices of the two subsystems, $\nu = 1$ and 2, respectively, are denoted by $\Lambda_\nu = \{\mathbf{a}^*_{\nu 1}, \mathbf{a}^*_{\nu 2}, \mathbf{a}^*_{\nu 3}\}$. Each subsystem has a one-dimensional modulation with wave vector $\mathbf{q}^{\nu'} = \mathbf{a}^*_{\nu 1}$ ($\nu' \neq \nu$).

All Bragg reflections can be indexed with four integer indices, $hklm$, based on the set of reciprocal vectors $M = \{\mathbf{a}^*_1, \mathbf{a}^*_2, \mathbf{a}^*_3, \mathbf{a}^*_4\}$. These vectors are defined as $\mathbf{a}^*_1 = \mathbf{a}^*_{11} = \mathbf{q}^2$, $\mathbf{a}^*_2 = \mathbf{a}^*_{12} = \mathbf{a}^*_{22}$, $\mathbf{a}^*_3 = \mathbf{a}^*_{13} = \mathbf{a}^*_{23}$ and $\mathbf{a}^*_4 = \mathbf{a}^*_{21} = \mathbf{q}^1$. It is then easily seen that $hkl0$ reflections comprise main reflections of the first subsystem, that $0klm$ reflections are main

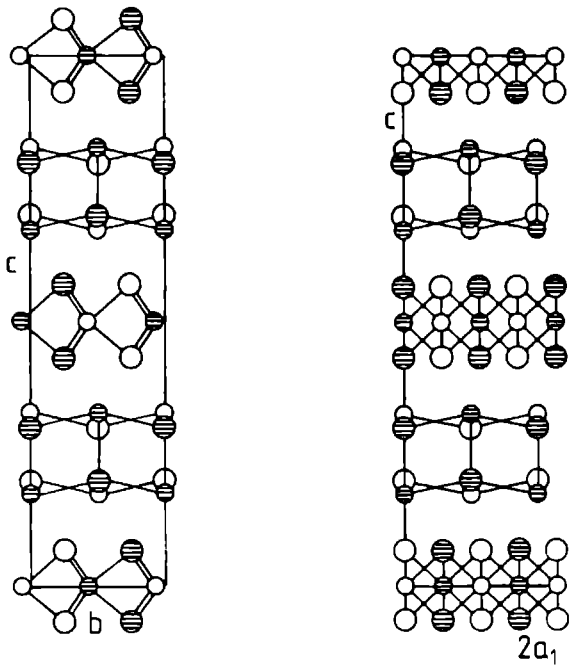


Figure 7.1. The structure of the inorganic misfit layer compound $(LaS)_{1.14}NbS_2$ Large circles denote sulfur atoms, small circles denote lanthanum and niobium in their respective subsystems Hatched and open circles differ by one-half in the projected coordinate (*a*) Projection along **a** (*b*) Projection along **b**

reflections of the second subsystem and that $hklm$ reflections ($h \neq 0$ and $m \neq 0$) are satellites X-ray diffraction intensities were measured by Meerschaut, Rabu & Rouxel, (1989) 860 unique reflections were obtained with intensities greater than 2 5 times their standard deviations There are 584 main reflections and 276 satellites The main reflections divide into 261 $hkl0$ reflections for the subsystem NbS_2 and 393 $0klm$ reflections for the subsystem LaS Both subsets include 70 $0kl0$ main reflections common to the subsystems

The method was also tested for $(PbS)_{1.18}TiS_2$, a compound similar to $(LaS)_{1.14}NbS_2$ but with monoclinic symmetry $C2_1/m(\alpha,0,0)1\bar{1}$ (van Smaalen, Meetsma, Wiegers & de Boer, 1991) For this compound, 500 $hkl0$ main reflections of subsystem TiS_2, 1131 $0klm$ main reflections of subsystem PbS and 190 satellite reflections are available Both main-reflection subsets now include 169 common $0kl0$ reflections The modulation is weaker than that in $(LaS)_{1.14}NbS_2$

(2) *Test for self-consistency among phases of main reflections*

Known phases of main reflections were substituted into the right-hand side of (7.3) to obtain new phases for the same set of main reflections on the left. The new phases were then compared with the original ones to check the self-consistency. This procedure corresponds to a single-step phase refinement. The results are listed in Table 7.1 for $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. For both structures, the phases of three different subsets of reflections were used as input. First, all the main reflections, $hkl0$ and $0klm$, were input into (7.3) to derive new phases for the same set. For the structure $(LaS)_{1.14}NbS_2$, this resulted in an average phase error of 10.5° for all main reflections and an error of 14.0° for only the $0kl0$ main reflections, which are common to both subsystems. Second, only the main reflections of subsystem 1, $hkl0$, were input into (7.3). For the structure $(LaS)_{1.14}NbS_2$ this resulted in an average error of 16.5° for all $hkl0$ reflections and an error of 32.7° for only the $0kl0$ reflections. Finally, only the main reflections of subsystem 2, $0klm$, were input into (7.3). The resulting phase error is 14.0° for all the $0klm$ reflections and 34.2° for only the $0kl0$ reflections. Similar results were obtained for the structure $(PbS)_{1.18}TiS_2$.

From the above test, it is seen that the self-consistency for phases of the complete set of four-dimensional main reflections is extremely good. One can expect that a four-dimensional direct-methods procedure could be used for *ab initio* determination of the four-dimensional basic structure. Besides, the self-consistency for phases of main reflections from either of the two subsystems is also reasonable, though it is not as good as that for the set of all main reflections. In particular, the agreement of the phases of the $0kl0$ reflections then becomes worse because the $0kl0$ reflections depend on both subsystems.

(3) *Test of ab initio phasing of satellite reflections*

Phases of satellite reflections were derived from the phases of the main reflections using (7.6). The main-reflection phases were obtained from the refinement of the basic structure. The resulting phases of satellites were compared with the corresponding phases obtained from the refined modulated structure (van Smaalen, 1991; van Smaalen *et al.*, 1991). It is seen that the phases from (7.6) are sufficiently accurate for the modulation to be revealed (Table 7.2). The best illustration for this statement is provided by the four-dimensional Fourier syntheses.

The principal part of the modulation in $(LaS)_{1.14}NbS_2$ is on lanthanum, with a first harmonic wave describing the displacement along $\mathbf{a}_{22}$ and a second harmonic wave displacement along $\mathbf{a}_{23}$. In $(PbS)_{1.18}TiS_2$, the modulation mainly resides on lead, with only a first harmonic defining displacements along $\mathbf{a}_{22}$. The La atom and the Pb atom are

Table 7.1. Test for the self-consistency of (7 3)

(*a*) $(LaS)_{1.14}NbS_2$

Reflections for which the phases are input into (7 3)		Reflections for which the phases are obtained from (7 3)		
Number of reflections	Index type of reflections	Number of reflections	Index type of reflections	Average phase error (°)
584	*hkl*0 and 0*klm*	584	*hkl*0 and 0*klm*	10 5
		70	0*kl*0	14 0
261	*hkl*0	261	*hkl*0	16 5
		70	0*kl*0	32 7
393	0*klm*	393	0*klm*	14 0
		70	0*kl*0	34 2

(*b*) $(PbS)_{1.18}TiS_2$

Reflections for which the phases are input into (7 3)		Reflections for which the phases are obtained from (7 3)		
Number of reflections	Index type of reflections	Number of reflections	Index type of reflections	Average phase error (°)
1462	*hkl*0 and 0*klm*	1462	*hkl*0 and 0*klm*	12 3
		169	0*kl*0	23 7
500	*hkl*0	500	*hkl*0	11 2
		169	0*kl*0	15 1
1131	0*klm*	1131	0*klm*	13 9
		169	0*kl*0	28 5

Table 7.2. Test of *ab initio* phasing of satellite reflections

Test structure	Number of main reflections input into (7 6)	Number of satellite reflections obtained from (7 6)	Average phase error (°)
$(LaS)_{1.14}NbS_2$	584	276	17 6
$(PbS)_{1.18}TiS_2$	1462	190	5 6

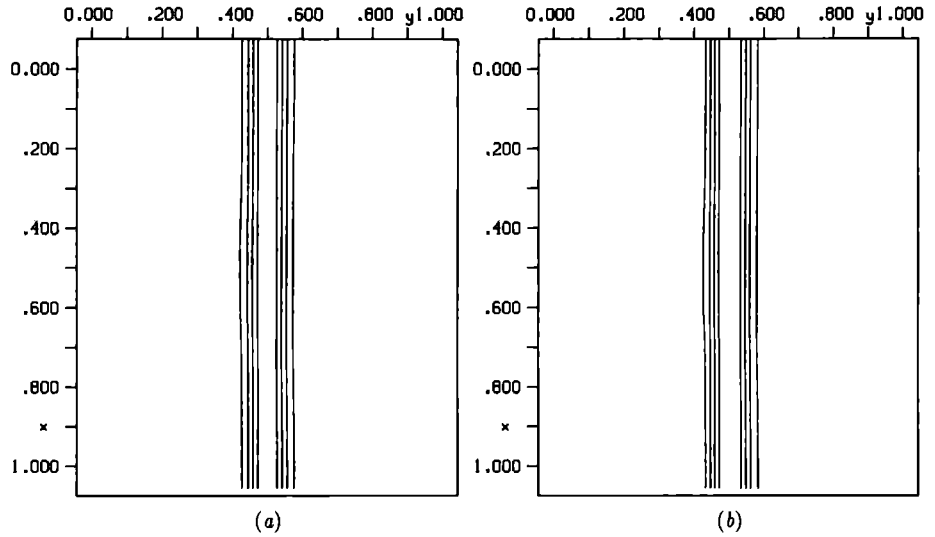


Figure 7.2. Section of the four dimensional Fourier synthesis of $(LaS)_{1.14}NbS_2$ at the position of the La atom ($x = 0$ and $z = 0.174$) Contours are plotted at intervals of 1/5 of the maximum density (*a*) Main reflections with phases from the basic structure refinement (*b*) Main reflections with phases from the modulated structure refinement

thus the best candidates for studying the effect of the modulation on the Fourier synthesis Here, we only discuss the results for lanthanum Completely equivalent results have been obtained for lead

The main reflections *hkl*0 contain the contribution from the *h*th-order satellites of the second subsystem and *vice versa* for the 0*klm* reflections This provides sufficient satellite information to refine the modulation, as was shown by Kato (1990) However, with only the main reflections, it is impossible to reveal the modulation directly in a Fourier synthesis This can be seen in the Fourier syntheses made for the main reflections with phases obtained from the basic structure refinement and from the modulated structure refinement, respectively (Figure 7 2), which show bands almost perfectly straight along $\bar{x}_4$ The reason is that the Fourier syntheses in Figure 7 2 can be expressed as

$$\int [F(hkl0)\exp(-2\pi i\mathbf{H}\ \ \mathbf{r}) + F(0klm)\exp(-2\pi i\mathbf{H}\ \ \mathbf{r})]\,\mathrm{d}\mathbf{H}\ \ = \mathcal{F}^{-1}[F(hkl0)] + \mathcal{F}^{-1}[F(0klm)],$$

where $\mathcal{F}^{-1}$ stands for the inverse Fourier transform The first term on the right-hand side is the projection of the four-dimensional electron-density function of the first subsystem

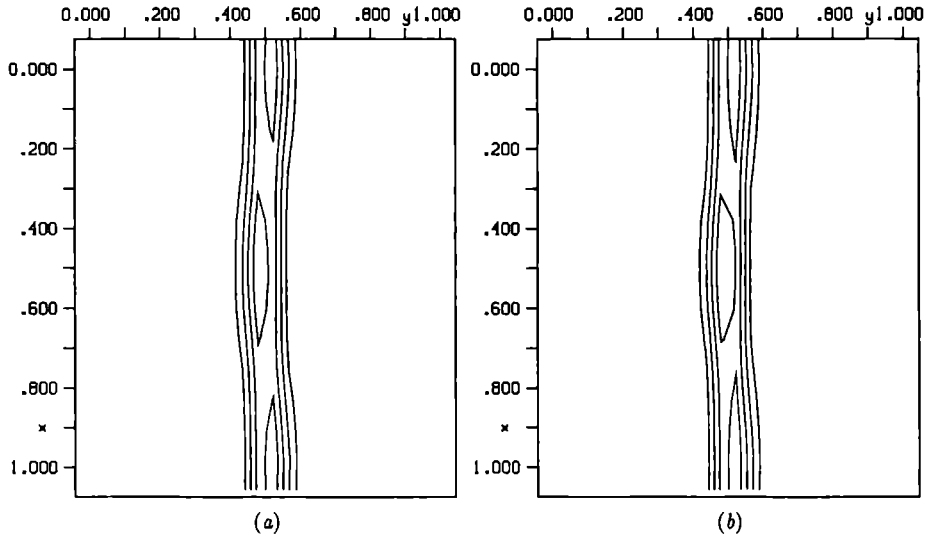


Figure 7.3. The same section of the four-dimensional Fourier synthesis as in Figure 7.2, now with both main reflections and satellites included (*a*) with phases from the refinement of the modulated structure, (*b*) with phases from the direct-methods procedure.

along its modulation direction $\bar{x}_4$, while the second term is the projection of the second subsystem along its modulation direction $\bar{x}_1$. Consequently, all modulation effects were averaged during the Fourier summation. This means that the modulation waves cannot be revealed directly by Fourier syntheses without involving satellite reflections. Figure 7.3 shows the Fourier syntheses of all reflections with the satellite reflections phased by the modulation refinement and by the direct method. It can be seen that the two Fourier syntheses are nearly the same and clearly show the modulation wave. This proves that the direct method can be successfully used to determine the modulation function for atoms of an incommensurate intergrowth compound.

7.4 Concluding remarks

For the first time, direct methods have successfully been used to determine the modulation in incommensurate intergrowth compounds. The procedure is straightforward and fully independent of any preliminary assumption of the modulation form. This provides a new more convenient and reliable approach to the study of modulation in intergrowth compounds. A new field has been opened for the application of direct methods.

References

HAO, Q., LIU, Y. W. & FAN, H. F. (1987). *Acta Cryst.* A**43**, 820–824.

JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* A**36**, 408–415.

KATO, K. (1990). *Acta Cryst.* B**46**, 39–44.

MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1989). *J. Solid State Chem.* **78**, 35–45.

MO, Y. D., CHENG, T. Z., FAN, H. F., LI, J. Q., SHA, B. D., ZHENG, C. D., LI, F. H. & ZHAO, Z. X. (1992). *Supercond. Sci. Technol.* **5**, 69–72.

SMAALEN, S. VAN (1991). *J. Phys. Condens. Matter*, **3**, 1247–1263.

SMAALEN, S. VAN (1992). *Mater. Sci. Forum*, **100&101**, 173–222.

SMAALEN, S. VAN, MEETSMA, A., WIEGERS, G. A. & DE BOER, J. L. (1991). *Acta Cryst.* B**47**, 314–325.

WIEGERS, G. A., MEETSMA, A., HAANGE, R. J., VAN SMAALEN, S., DE BOER, J. L., MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1990). *Acta Cryst.* B**46**, 324–332.

XIANG, S. B., FAN, H. F., WU, X. J., LI, F. H. & PAN, Q. (1990). *Acta Cryst.* A**46**, 929–934.

8

Direct Methods for Incommensurate Intergrowth Compounds. II. Determination of the Modulation using only Main Reflections*

Abstract

A modified Sayre equation for incommensurate intergrowth compounds is presented. With this equation, both magnitude and phase for structure factors of satellite reflections can be estimated quantitatively through the observed intensities of main reflections, provided their phases are already known. Modulation functions can then be revealed by the Fourier synthesis calculated using the observed main reflections and the estimated satellites. The method has been tested with the known structures of two inorganic misfit layer compounds, $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. Satisfactory results were obtained.

*Published as: Sha, B. D., Fan, H. F., Smaalen, S. van, Lam, E. J. W. & Beurskens, P. T. (1994). *Acta Crystallographyca*, **A50**, 511–515.

8.1 Introduction

Incommensurate intergrowth compounds can be considered as coherent combinations of two or more modulated structures (Janner & Janssen, 1980; van Smaalen, 1992). In a diffraction experiment, they give Bragg reflections at the nodes of the reciprocal lattices of the basic structures of the subsystems (main reflections). Additional, satellite, reflections are found owing to the incommensurate modulations. In paper I of this series (Fan, van Smaalen, Lam & Beurskens, 1993), the multidimensional direct method proposed by Hao, Liu & Fan (1987) has been extended for use in the determination of modulations in composite structures. Experimentally observed intensities of both main and satellite reflections are needed in this procedure. However, because intensities of main reflections contain information on the modulation, it could be possible to determine the modulation in a composite structure by measuring only the intensities of main reflections. For this purpose, a new modified Sayre equation is derived, with which the magnitudes and phases for structure factors of satellite reflections can be estimated quantitatively, provided the magnitudes and phases of the main reflections are known. A least-squares method has been used to determine the modulation of composite structures using only the observed structure-factor magnitudes of main reflections (Kato, 1990). Our method differs from the least-squares method in that the structure factors of satellites can be estimated before the modulation model has been established. This means that with our method the modulation waves can be measured directly from the resultant Fourier map while no preliminary assumption about the modulation is needed.

8.2 The method

1. *Modified Sayre equations for composite structures*

According to the structure-factor formula for a composite structure of incommensurate intergrowth compounds (Petříček, Maly, Coppens, Bu, Cisarova & Frost-Jensen, 1991; van Smaalen, 1992; Yamamoto, 1992), we can define the structure factor for a composite structure, $\mathcal{F}(\mathbf{H_s})$, as

$$\mathcal{F}(\mathbf{H_s}) = \sum_{\nu} F_\nu(\mathbf{H_s} W^{\nu,-1})/V_\nu, \tag{8.1}$$

where V_ν and $F_\nu(\mathbf{H_s})$ are, respectively, the unit-cell volume and the structure factor of the νth substructure; $\mathbf{H_s} = (h_1, \ldots, h_{3+d})$ is the $(3+d)$-dimensional scattering vector; and the matrices W^ν take care of the fact that the role of main-reflection indices and satellite indices is different for the different subsystems ν (van Smaalen, 1992). As a single unit

cell is not defined, the structure factor (8.1) is normalized to scattering per unit volume of material, *e.g.* per Å^3. If $\mathbf{H}_s^\nu = \mathbf{H}_s W^{\nu,-1}$, then $F_\nu(\mathbf{H}_s^\nu)$ can be expressed as (Yamamoto, 1982)

$$\begin{aligned} F_\nu(\mathbf{H}_s^\nu) &= \sum_{(R_s^\nu|\tau_s^\nu)} \sum_\mu mt_\mu \int_0^1 \mathrm{d}t_1 \ldots \int_0^1 \mathrm{d}t_d \, P^\mu(\mathbf{t}) f_\mu(\mathbf{H}_s^\nu) \times \\ &\quad \exp\{2\pi i[\mathbf{H}_3^\nu \cdot R_3^\nu \cdot \mathbf{x}^0(\mu) + \mathbf{H}_d^\nu \cdot M_{d3}^\nu \cdot \mathbf{x}^0(\mu) + \\ &\quad \mathbf{H}_s^\nu \cdot \tau_s^\nu + \mathbf{H}^\nu \cdot R_3^\nu \cdot \mathbf{u}^\mu(\mathbf{t}) + \mathbf{H}_d^\nu \cdot R_d^\nu \cdot \mathbf{t}]\}, \end{aligned} \tag{8.2}$$

where

$$f_\mu(\mathbf{H}_s^\nu) = f_\mu^0(|\mathbf{H}^\nu|) \exp[-\tilde{\mathbf{H}}^\nu \cdot \tilde{R}_3^\nu \cdot \underline{\beta}^\mu(\mathbf{t}) \cdot R_3^\nu \cdot \mathbf{H}^\nu]. \tag{8.3}$$

mt_μ is the multiplicity factor of the independent atom μ of subsystem ν. f_μ^0 and $\underline{\beta}^\mu$ are the three-dimensional atomic scattering factor and temperature factor of the μth atom, respectively. $\mathbf{H}^\nu$ is the projection of $\mathbf{H}_s^\nu$ onto physical space while $\mathbf{H}_3^\nu$ and $\mathbf{H}_d^\nu$ represent, respectively, the first three and the last d components of $\mathbf{H}_s^\nu$. The subsystem symmetry operators $(R_s^\nu|\tau_s^\nu)$ are derived from superspace symmetry operators $(R_s|\tau_s)$ by application of W^ν. They are composed of a 3×3 physical-space part (R_3^ν), a $d \times d$ part transforming the additional coordinates and the left lower $d \times 3$ part M_{d3}^ν. The right upper $3 \times d$ part only contains zero's. $\tilde{M}$ indicates the transpose of the matrix M. The atomic positions are divided into a basic-structure position $\mathbf{x}^0(\mu)$ and a modulation part $\mathbf{u}^\mu(\bar{x}_{\nu s,4}, \ldots, \bar{x}_{\nu s,3+d})$, with arguments of the modulation functions $\bar{\mathbf{x}}_{\nu s,3+j} = \sigma_\nu[\mathbf{L}+\mathbf{x}^0(\mu)]$, where σ_ν is the matrix of modulation wave vectors for subsystem ν and $\mathbf{L}$ is a lattice vector of the basic structure. The occupational probability $P(\bar{x}_{\nu s,4}, \ldots, \bar{x}_{\nu s,3+d})$ and the temperature tensor may also be modulated. Equations (8.1)–(8.3) are easily generalized to include symmetry operators that map one subsystem onto another (van Smaalen, 1992).

Similarly to three-dimensional space, we have in multidimensional space

$$\rho_s(\mathbf{x}_s) = \sum_{\mathbf{H}_s} \mathcal{F}(\mathbf{H}_s) \exp(-2\pi i \mathbf{H}_s \cdot \mathbf{x}_s) \tag{8.4}$$

and

$$\mathcal{F}^{sq}(\mathbf{H}_s) = \sum_{\mathbf{H}_s'} \mathcal{F}(\mathbf{H}_s') \mathcal{F}(\mathbf{H}_s - \mathbf{H}_s'), \tag{8.5}$$

where $\mathcal{F}^{sq}(\mathbf{H}_s)$ is the structure factor of the squared multidimensional structure in which atoms are squared while their positional parameters are left unchanged. Corresponding to (8.1), (8.2) and (8.3), we have

$$\mathcal{F}^{sq}(\mathbf{H}_s) = \sum_\nu F_\nu^{sq}(\mathbf{H}_s W^{\nu,-1})/V_\nu, \tag{8.6}$$

$$F_\nu^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}^\nu) = \sum_{(R_\mathrm{s}^\nu|\tau_\mathrm{s}^\nu)} \sum_\mu m t_\mu \int_0^1 \mathrm{d}t_1 \ldots \int_0^1 \mathrm{d}t_d [P^\mu(\mathbf{t})]^2 f_\mu^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}^\nu) \times$$
$$\exp\{2\pi i[\mathbf{H}_3^\nu \cdot R_3^\nu \cdot \mathbf{x}^0(\mu) + \mathbf{H}_d^\nu \cdot M_{d3}^\nu \cdot \mathbf{x}^0(\mu) +$$
$$\mathbf{H}_\mathrm{s}^\nu \cdot \boldsymbol{\tau}_\mathrm{s}^\nu + \mathbf{H}^\nu \cdot R_3^\nu \cdot \mathbf{u}^\mu(\mathbf{t}) + \mathbf{H}_d^\nu \cdot R_d^\nu \cdot \mathbf{t}]\} \tag{8.7}$$

and

$$f_\mu^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}^\nu) = f_\mu^{\mathrm{sq},0}(|\mathbf{H}^\nu|) \exp[-\tilde{\mathbf{H}}^\nu \cdot \tilde{R}_3^\nu \cdot \underline{\beta}^{\mu,\mathrm{sq}}(\mathbf{t}) \cdot R_3^\nu \cdot \mathbf{H}^\nu], \tag{8.8}$$

where $f_\mu^{\mathrm{sq},0}(|\mathbf{H}^\nu|)$ and $\underline{\beta}^{\mu,\mathrm{sq}}$ denote the three-dimensional atomic scattering factor and temperature factor of the μth squared nonequivalent atom in subsystem ν, respectively.

Suppose that the crystal is composed of equal atoms and $P^\mu(\bar{x}_{\nu\mathrm{s},4}, \ldots, \bar{x}_{\nu\mathrm{s},3+d}) \simeq 1$. Also, assume that the temperature tensor is not modulated. Then, $f_\mu(\mathbf{H}_\mathrm{s}^\nu) = f(\mathbf{H}_\mathrm{s})$ and $f_\mu^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}^\nu) = f^{\mathrm{sq}}(\mathbf{H}_\mathrm{s})$ and it follows from (8.1), (8.2), (8.6) and (8.7) that

$$\mathcal{F}(\mathbf{H}_\mathrm{s}) = f(\mathbf{H}_\mathrm{s}) A(\mathbf{H}_\mathrm{s}) \tag{8.9}$$

and

$$\mathcal{F}^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}) = f^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}) A(\mathbf{H}_\mathrm{s}), \tag{8.10}$$

where

$$A(\mathbf{H}_\mathrm{s}) = \sum_\nu V_\nu^{-1} \sum_{(R_\mathrm{s}^\nu|\tau_\mathrm{s}^\nu)} \sum_\mu m t_\mu \int_0^1 \mathrm{d}t_1 \ldots \int_0^1 \mathrm{d}t_d \times$$
$$\exp\{2\pi i[\mathbf{H}_3^\nu \cdot R_3^\nu \cdot \mathbf{x}^0(\mu) + \mathbf{H}_d^\nu \cdot M_{d3}^\nu \cdot \mathbf{x}^0(\mu) +$$
$$\mathbf{H}_\mathrm{s}^\nu \cdot \boldsymbol{\tau}_\mathrm{s}^\nu + \mathbf{H}^\nu \cdot R_3^\nu \cdot \mathbf{u}^\mu(\mathbf{t}) + \mathbf{H}_d^\nu \cdot R_d^\nu \cdot \mathbf{t}]\}. \tag{8.11}$$

Hence,

$$\mathcal{F}(\mathbf{H}_\mathrm{s})/\mathcal{F}^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}) = f(\mathbf{H}_\mathrm{s})/f^{\mathrm{sq}}(\mathbf{H}_\mathrm{s}) = \theta(\mathbf{H}_\mathrm{s}). \tag{8.12}$$

Combining (8.5) and (8.12), we obtain

$$\mathcal{F}(\mathbf{H}_\mathrm{s}) = \theta(\mathbf{H}_\mathrm{s}) \sum_{\mathbf{H}_\mathrm{s}'} \mathcal{F}(\mathbf{H}_\mathrm{s}') \mathcal{F}(\mathbf{H}_\mathrm{s} - \mathbf{H}_\mathrm{s}'). \tag{8.13}$$

This is the multidimensional Sayre equation for composite structures. The right-hand side of (8.13) can be divided into three parts, then

$$\mathcal{F}(\mathbf{H}_\mathrm{s}) = \theta(\mathbf{H}_\mathrm{s}) \left[\sum_{\mathbf{H}_\mathrm{s}'} \mathcal{F}_{\mathrm{main}}(\mathbf{H}_\mathrm{s}') \mathcal{F}_{\mathrm{main}}(\mathbf{H}_\mathrm{s} - \mathbf{H}_\mathrm{s}') + \right.$$

$$2\sum_{\mathbf{H}'_s}\mathcal{F}_{\rm main}(\mathbf{H}'_s)\mathcal{F}_{\rm sat}(\mathbf{H}_s-\mathbf{H}'_s)+$$

$$\sum_{\mathbf{H}'_s}\mathcal{F}_{\rm sat}(\mathbf{H}'_s)\mathcal{F}_{\rm sat}(\mathbf{H}_s-\mathbf{H}'_s)\Bigg], \tag{8.14}$$

where the subscript 'main' indicates main reflections and the subscript 'sat' indicates satellites.

First consider $\mathbf{H}_s$ in (8.14) to be a satellite reflection. Because, on average, the intensity of satellites is much weaker than that of main reflections, the last two summations on the right-hand side of (8.14) are much smaller than the first. Neglecting those, we have the modified Sayre equation relating satellite reflections to main reflections:

$$\mathcal{F}_{\rm sat}(\mathbf{H}_s)\simeq\theta_{\rm sat}(\mathbf{H}_s)\sum_{\mathbf{H}'_s}\mathcal{F}_{\rm main}(\mathbf{H}'_s)\mathcal{F}_{\rm main}(\mathbf{H}_s-\mathbf{H}'_s). \tag{8.15}$$

On the other hand, if $\mathbf{H}_s$ corresponds to a main reflection, two of the three contributions to (8.14) are retained to obtain another modified Sayre equation:

$$\mathcal{F}_{\rm main}(\mathbf{H}_s)\simeq\theta_{\rm main}(\mathbf{H}_s)\Bigg[\sum_{\mathbf{H}'_s}\mathcal{F}_{\rm main}(\mathbf{H}'_s)\mathcal{F}_{\rm main}(\mathbf{H}_s-\mathbf{H}'_s)+$$

$$2\sum_{\mathbf{H}'_s}\mathcal{F}_{\rm main}(\mathbf{H}'_s)\mathcal{F}_{\rm sat}(\mathbf{H}_s-\mathbf{H}'_s)\Bigg]; \tag{8.16}$$

although the second term is small compared to the first, it is retained to allow calculation of the influence of the satellite reflections on the main reflections.

2. *Determination of the function* $\theta(\mathbf{H}_s)$

Equation (8.15) implies that both the magnitude and phase of the structure factor for satellite reflections can be estimated from the whole set of structure factors of main reflections, of which magnitudes are measured from the experiment while phases can be calculated from the known basic structure. However, there remains the problem of determining the function $\theta(\mathbf{H}_s)$. For an equal-atom structure, $\theta(\mathbf{H}_s)$ can be calculated from (8.12) using the form factor of the squared structure, which is easily calculated by the convolution

$$f_0^{\rm sq}(|\mathbf{H}|)=\int f_0(|\mathbf{H}'|)f_0(|\mathbf{H}-\mathbf{H}'|)\,{\rm d}\mathbf{H}'. \tag{8.17}$$

For nonequal-atom structures, $\theta(\mathbf{H_s})$ is approximated by its weighted average:

$$\theta(\mathbf{H_s}) \simeq \left\{ \frac{\sum_\mu w_\mu [f_\mu^0(|\mathbf{H}|)]^2}{\sum_\mu w_\mu [f_\mu^{\mathrm{sq},0}(|\mathbf{H}|)]^2} \right\}^{1/2}, \tag{8.18}$$

where the weights represent the amount of atom type μ present in the structure [*e.g.* for $(LaS)_{1.14}NbS_2$ the weights are $w(La)=1.14$, $w(Nb)=1$ and $w(S)=3.14$)].

In practice, $\theta(\mathbf{H_s})$ will not be given by (8.12). The functions that enter the Sayre equation [(8.13)–(8.16)] depend on the temperature factors, which are not known. Furthermore, series-termination effects heavily influence the values of the summations and the Σ_2 relationships involved are different for (8.15) and (8.16). Therefore, $\theta_{\mathrm{sat}}(\mathbf{H_s})$ in (8.15) is not equal to $\theta_{\mathrm{main}}(\mathbf{H_s})$ in (8.16) and they both need to be determined from experimental data. The combination of (8.15) and (8.16) gives

$$\begin{aligned} \mathcal{F}_{\mathrm{main}}(\mathbf{H_s}) \simeq \theta_{\mathrm{main}}(\mathbf{H_s}) \Bigg\{ & \sum_{\mathbf{H_s'}} \mathcal{F}_{\mathrm{main}}(\mathbf{H_s'}) \mathcal{F}_{\mathrm{main}}(\mathbf{H_s} - \mathbf{H_s'}) + \\ & 2 \sum_{\mathbf{H_s'}} \Bigg[\mathcal{F}_{\mathrm{main}}(\mathbf{H_s'}) \theta_{\mathrm{sat}}(\mathbf{H_s} - \mathbf{H_s'}) \times \\ & \sum_{\mathbf{H_s''}} \mathcal{F}_{\mathrm{main}}(\mathbf{H_s''}) \mathcal{F}_{\mathrm{main}}(\mathbf{H_s} - \mathbf{H_s'} - \mathbf{H_s''}) \Bigg] \Bigg\}. \end{aligned} \tag{8.19}$$

Equation (8.19) can be used to estimate $\theta_{\mathrm{sat}}(\mathbf{H_s})$ and $\theta_{\mathrm{main}}(\mathbf{H_s})$ because it involves only structure factors of main reflections, which are assumed to be known in advance. $\theta_{\mathrm{sat}}(\mathbf{H_s})$ and $\theta_{\mathrm{main}}(\mathbf{H_s})$ are each in fact some kind of atomic form factors. They may be expressed as the sum of Gaussian functions. We write accordingly

$$\theta_{\mathrm{main}}(\mathbf{H_s}) = \sum_i A_i^{\mathrm{main}} \exp(-B_i^{\mathrm{main}} |\mathbf{H}|^2) + C^{\mathrm{main}} \tag{8.20}$$

and

$$\theta_{\mathrm{sat}}(\mathbf{H_s}) = \sum_i A_i^{\mathrm{sat}} \exp(-B_i^{\mathrm{sat}} |\mathbf{H}|^2) + C^{\mathrm{sat}}, \tag{8.21}$$

where only terms with $i = 1, 2$ have been used. All the parameters A_i^{sat}, B_i^{sat}, C^{sat}, A_i^{main}, B_i^{main} and C^{main} can be obtained by a least-squares refinement based on (8.19). It should be noted that, if $\theta_{\mathrm{sat}}(\mathbf{H_s})$ and $\theta_{\mathrm{main}}(\mathbf{H_s})$ are determined by a fit to (8.19), using $|F_o|$, their absolute values represent the scale of the experimental data and thus have no physical meaning. Only the angle dependence and their relative values can have some meaning.

Table 8.1. Coefficients of the function $\theta_{\rm main}$

Sample	$A_1^{\rm main}$ $\times 10^{-6}$	$A_2^{\rm main}$ $\times 10^{-6}$	$B_1^{\rm main}$	$B_2^{\rm main}$	$C^{\rm main}$ $\times 10^{-6}$
$(LaS)_{1.14}NbS_2$	2.956	8.871	0.2550	−0.2518	−2.176
$(PbS)_{1.18}TiS_2$	4.773	−0.2279	0.2426	4.9440	−1.234

Table 8.2. Coefficients of the function $\theta_{\rm sat}$

Sample	$A_1^{\rm sat}$ $\times 10^{-6}$	$A_2^{\rm sat}$ $\times 10^{-6}$	$B_1^{\rm sat}$	$B_2^{\rm sat}$	$C^{\rm sat}$ $\times 10^{-6}$
$(LaS)_{1.14}NbS_2$	98.98	107.7	0.2233	0.1357	106.2
$(PbS)_{1.18}TiS_2$	60.13	3.033	0.3101	2.0549	0.3021

8.3 Test and results

The method was tested with experimental X-ray diffraction data of $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$ (van Smaalen, 1991; van Smaalen, Meetsma, Wiegers & de Boer, 1991). Both structures can be described as an alternating stacking of two types of layers (Wiegers & Meerschaut, 1992; van Smaalen, 1992). For $(LaS)_{1.14}NbS_2$, there are in total 860 unique reflections with 584 main reflections and 276 satellites; while for $(PbS)_{1.18}TiS_2$, 1652 unique reflections, including 1462 main reflections and 190 satellites, are available.

First, coefficients for the expressions of $\theta_{\rm main}(\mathbf{H}_s)$ and $\theta_{\rm sat}(\mathbf{H}_s)$ were determined by a least-squares refinement based on (8.19) using the known phases and experimentally measured structure-factor magnitudes of main reflections. Results are listed in Tables 8.1 and 8.2. The reliability of these coefficients was checked by calculating the R factors

$$R = \frac{\sum ||\mathcal{F}_o| - |\mathcal{F}_c||}{\sum |\mathcal{F}_o|}, \tag{8.22}$$

where $|\mathcal{F}_o|$ is the structure factor magnitude of main reflections derived from the experiment and satisfying the definition of (8.1), $|\mathcal{F}_c|$ is that calculated from (8.19). We found that the final R factor for 584 main reflections of $(LaS)_{1.14}NbS_2$ is 0.233, while that for 1462 main reflections of $(PbS)_{1.18}TiS_2$ is 0.399.

Phases and moduli of satellite reflections were then calculated by phases and moduli of main reflections and $\theta_{\rm sat}(\mathbf{H}_s)$ input into (8.15). For $(LaS)_{1.14}NbS_2$, the average phase error with the phases from the refinement of the modulated structures is the same as obtained with the phase-extension procedure (Fan, van Smaalen, Lam & Beurskens, 1993). For $(PbS)_{1.18}TiS_2$, the average phase error is slightly larger (Table 8.3). Comparing observed

Table 8.3. Comparison of satellite structure factors obtained by direct methods [(8 15)] with measured amplitudes of the satellites and phases from the modulated structure refinement

R is defined in (8 22)

Sample	Number of reflections	Average phase error (°)	R
$(LaS)_{1.14}NbS_2$	276	17 05	0 300
$(PbS)_{1.18}TiS_2$	190	8 84	0 197

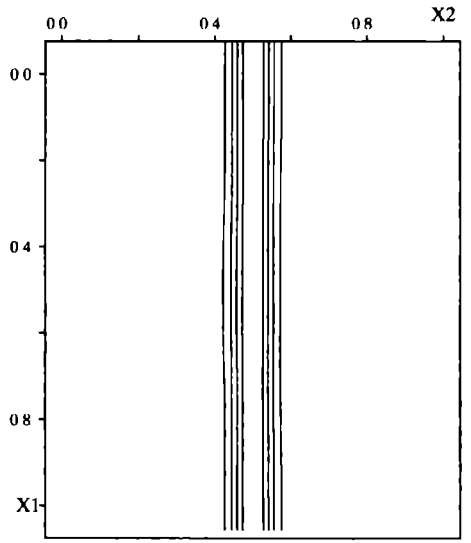


Figure 8.1. Section of the four dimensional Fourier synthesis of $(LaS)_{1.14}NbS_2$ at the position of the La atom ($x = 0$ and $z = 0.174$) Contours are plotted at intervals of 1/5 of the maximum density Main reflections are used, with experimental magnitudes and phases from the basic-structure refinement

magnitudes with the calculated magnitudes of the satellites gives a higher R factor than the partial R factor in the refinement It is to be determined whether the calculated satellites can be used in a refinement procedure Nevertheless, Fourier maps do show the usefulness of the calculated satellite structure factors The Fourier synthesis at the position of lanthanum using main reflections only does not show the modulation (Figure 8 1) The additional inclusion of the calculated satellite structure factors (8 15) gives a Fourier map that is indistinguishable from the Fourier map obtained with measured magnitudes and phases from the refinement (Figures 8 2 and 8 3)

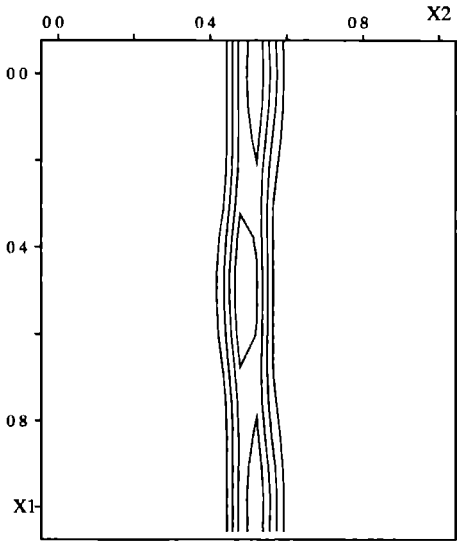


Figure 8.2. The same section of the four-dimensional Fourier synthesis as in Figure 8 1 Experimental main reflections with phases from the basic-structure refinement are combined with both magnitudes and phases of satellite reflections obtained with the direct-methods procedure [(8 15)]

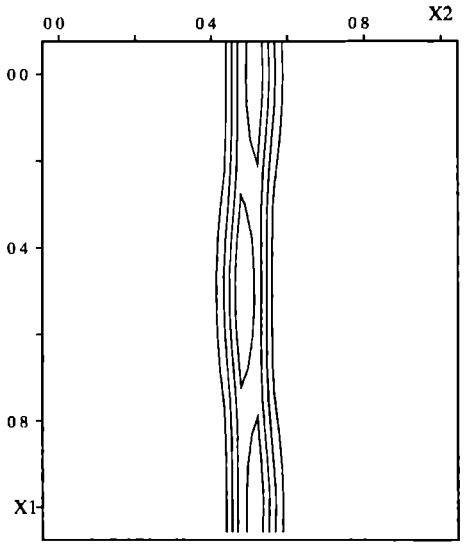


Figure 8.3. The same section of the four-dimensional Fourier synthesis as in Figure 8 1 For both main reflections and satellites, structure factors are used with experimental magnitudes and phases from the modulated-structure refinement

8.4 Concluding remarks

It was shown previously that satellite reflections are an essential ingredient to make the modulations visible in a Fourier synthesis of the reflections of an incommensurate intergrowth compound (Fan, van Smaalen, Lam & Beurskens, 1993) In this paper, it is shown that both the magnitudes and the phases of the satellite reflections can be derived from the structure factors of the main reflections For the latter, measured amplitudes are combined with phases obtained from, for example, a basic-structure refinement, or a direct-methods procedure independent of the satellite reflections This, at first sight surprising, result can be understood from the special nature of intergrowth compounds The two subsystems coexist in a single thermodynamic phase and part of the satellite intensity due to the modulation is already contained in the main reflections This information allowed the refinement of modulation parameters on main reflections only (Kato, 1990), but it is insufficient to reveal the modulation amplitudes in a Fourier synthesis (Figure 8 1)

The method proposed here allows one to calculate the satellite structure factors from the main reflections with sufficient accuracy to determine the modulation from a Fourier map (Figure 8.2).

Phases of the satellite reflections can be obtained as described earlier (Fan, van Smaalen, Lam & Beurskens, 1993). For their magnitudes to be determined, a crucial step is that the functions $\theta_{\rm sat}(\mathbf{H_s})$ and $\theta_{\rm main}(\mathbf{H_s})$ can both be determined from the main reflections alone [(8.15), (8.16) and (8.19)]. Applications are given to the inorganic misfit layer compounds $(LaS)_{1.14}NbS_2$ and $(PbS)_{1.18}TiS_2$. The Fourier map calculated with the main reflections and the satellite reflections generated in the direct-methods procedure is found to be indistinguishable from the Fourier synthesis using experimental amplitudes for all reflections combined with phases from the refinement (Figures 8.2 and 8.3). This shows the structure factors of the satellite reflections calculated with (8.15) to be sufficiently accurate to determine the modulations in these composite crystals.

References

Fan, H. F., van Smaalen, S., Lam, E. J. W. & Beurskens, T. (1993). *Acta Cryst.* A**49**, 704–708.

Hao, Q., Liu, Y. W. & Fan, H. F. (1987). *Acta Cryst.* A**43**, 820–824.

Janner, A. & Janssen, T. (1980). *Acta Cryst.* A**36**, 408–415.

Kato, K. (1990). *Acta Cryst.* B**46**, 39–44.

Petříček, V., Maly, K., Coppens, P., Bu, X., Cisarova, I. & Frost-Jensen, A. (1991). *Acta Cryst.* A**47**, 210–216.

Smaalen, S. van (1991). *J. Phys. Condens. Matter*, **3**, 1247–1263.

Smaalen, S. van (1992). *Mater. Sci. Forum*, **100&101**, 173–222.

Smaalen, S. van, Meetsma, A., Wiegers, G. A. & de Boer, J. L. (1991). *Acta Cryst.* B**47**, 314–325.

Wiegers, G. A. & Meerschaut, A. (1992). *Mater. Sci. Forum*, **100&101**, 101–172.

Yamamoto, A. (1982). *Acta Cryst.* A**38**, 87–92.

Yamamoto, A. (1992). *Acta Cryst.* A**48**, 476–483.

9

Ab Initio Solution of Misfit Layer Structures by Automatic Patterson and Direct Methods*

Abstract

A procedure is presented for the automatic solution of composite (misfit) layer compounds, for the case when the composite crystal structure consists of two types of layer, each of which can be approximately described as a three-dimensional periodic structure with, however, mutually incommensurate lattices and hence mutually induced incommensurate modulations. The composite structure can be described as a periodic structure in four-dimensional superspace [van Smaalen (1992), *Mater. Sci. Forum*, **100&101**, 173–222]. From reflection data indexed with four integer indices $HKLM$, the phase problem is solved as follows. The basic structures of layers 1 and 2 are solved by routine application of automated Patterson interpretation and Fourier recycling using the main reflections only and ignoring the modulation effects. The two layers are brought to a common origin by a shift function based on correlating $F_{\rm obs}$ and $F_{\rm calc}$ using the main reflections common to both layers. All other reflections, which are the (usually weaker) satellite reflections, are phased from the known phases of the main reflections of either layer by application of the Sayre equation in four-dimensional superspace [Hao, Liu & Fan (1987), *Acta Cryst.* A**43**, 820–824; Fan, van Smaalen, Lam & Beurskens (1993), *Acta Cryst.* A**49**, 704–708]. The procedure is performed by the program *MISFIT*, which is embedded in the *DIRDIF* system.

*Published as: Beurskens, P. T., Beurskens, G., Lam, E. J. W., Smaalen, S. van & Fan, H.-F. (1994). *Journal of Applied Crystallography*, **27**, 411–417.

9.1 Introduction

A misfit layer compound is an incommensurate intergrowth compound consisting of two or more types of layer. Each type of layer (or substructure) can be approximately described as a three-dimensional periodic structure with, however, mutually incommensurate lattices and hence mutually induced incommensurate modulations. A survey of such structures has recently been given by Wiegers & Meerschaut (1992). The composite structure is best described as a periodic structure in higher-dimensional space (Janner & Janssen, 1980; van Smaalen, 1992). So far, only composite layer structures with two different types of layer and with just one incommensurate axial direction are known, so we restrict the discussion to the four-dimensional case: each substructure is characterized by a unit cell and a modulation wave vector, which is a basic reciprocal-lattice vector of the other substructure.

A direct-methods procedure for the solution of such structures has been described in a previous paper (Fan, van Smaalen, Lam & Beurskens, 1993, hereinafter denoted Ref. I), where it is shown that the modified Sayre equation for four-dimensional superspace (Hao, Liu & Fan, 1987) is applicable to composite structures. The *ab initio* application of this method is being programmed (Fu & Fan, 1994).

As all misfit layer structures known so far contain heavy atoms, an obvious strategy is to start the structural investigations by the application of heavy-atom Patterson-interpretation procedures for the solution of the two basic structures, which indeed has been the case up to date (Wiegers & Meerschaut, 1992). Once the basic structures are known, the relative positions of the two layers have to be established from the observed intensity data of the reflections common to the two layers. In the present procedure, we follow this strategy up to this point. Subsequent determination of the modulation parameters, which describe the modulations caused by the mutual interactions of the two layers, is usually carried out by trial and error. In the present procedure, the phasing of the satellite reflections is accomplished by the application of direct methods in four-dimensional superspace (Ref. I). Thus, an automatic solution of the phase problem of misfit layer compounds is obtained in four steps (Sections 9.2 9.4).

(i) The basic structure of layer 1 is solved by Patterson methods.

(ii) The basic structure of layer 2 is solved by Patterson methods.

(iii) The two layers are brought to a common origin by a shift function.

(iv) The phases of the satellites are found by direct methods.

These four steps are executed by the program *MISFIT*. Details of which are given in Section 9.5. After the phase problem has been solved this way, the phased structure factors are input to a program for a four-dimensional Fourier synthesis and further structure analysis.

Nomenclature

A general formalism for composite structures and the embedding of substructures in higher-dimensional superspace has been given by van Smaalen (1992). We restrict the nomenclature to the four-dimensional case of misfit layer structures consisting of two incommensurate layers.

The reflection data are indexed with four integer indices $HKLM$, which refer to the set of reciprocal-lattice vectors ($\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$, $\mathbf{a}_4^*$). In the present setting, the two substructures have $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ in common. The basic lattice periodicities of substructure ν ($\nu = 1$ or 2) are denoted $\mathbf{a}_{\nu 1}$, $\mathbf{a}_{\nu 2}$, $\mathbf{a}_{\nu 3}$. The parallel and incommensurate basic vectors are $\mathbf{a}_{11}$ and $\mathbf{a}_{21}$. When considering individual basic structures, we use conventional notation, *e.g.* unit cell **a**, **b**, **c**. The basic structure of layer 1 is associated with the *main* reflections $HKL0$ of the composite structure: $hkl = HKL$, reciprocal lattice ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$) = ($\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$) and (by inversion) unit cell (**a**, **b**, **c**) = ($\mathbf{a}_{11}$, $\mathbf{a}_{12}$, $\mathbf{a}_{13}$). The basic structure of layer 2 is associated with the *main* reflections $0KLM$ of the composite structure: $hkl = MKL$, reciprocal lattice ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$) = ($\mathbf{a}_4^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$) and unit cell (**a**, **b**, **c**) = ($\mathbf{a}_{21}$, $\mathbf{a}_{22}$, $\mathbf{a}_{23}$). The reflections $HKLM$ ($H \neq 0$, $M \neq 0$) are the (usually weaker) *satellite* reflections. The special reflections $0KL0$ are the main reflections common to both substructures.

The three-dimensional unit cell of a basic structure may conveniently be transformed to any other setting; the three-dimensional main reflections are then transformed accordingly. For this purpose, we define the matrices B_ν, which transform reflection indices $HKLM$ into indices for the desired settings of the three-dimensional modulated substructures.

$$\begin{aligned} \text{Layer 1,} \quad & hkl0 = HKL0 \cdot B_1; \\ \text{layer 2,} \quad & hkl0 = 0KLM \cdot B_2; \end{aligned} \tag{9.1}$$

with, of course, corresponding transformation of the basic unit cells. The matrix B_ν is the inverse of the matrix W^ν defined by van Smaalen (1992).

Examples

Details of the procedure are illustrated for the structure of $(LaS)_{1.14}NbS_2$ and, in less detail, for the structure of $(PbS)_{1.18}TiS_2$, using the code names LANBS and PBTIS (see

Table 9.1. Crystal data for the two test compounds

For these examples, the **b** and **c** translations are common to the two subsystems.

(a) LANBS = $(LaS)_{1.14}NbS_2$

Layer 1 NbS_2; space group $Fm2m$
$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_{11}, \mathbf{a}_{12}, \mathbf{a}_{13})$
Unit cell: 3.310, 5.793, 23.043 Å

Layer 2 LaS; space group $Cm2a$
$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_{21}, \mathbf{a}_{22}, \frac{1}{2}\mathbf{a}_{13})$
Unit cell: 5.828, 5.793, 11.5215 Å (half-length **c** axis)

(b) PBTIS = $(PbS)_{1.18}TiS_2$

Layer 1 TiS_2; space group $C2/m$
$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_{11}, \mathbf{a}_{12}, \mathbf{a}_{13})$, **a** axis unique
Unit cell: 3.409, 5.881, 11.670 Å, $\alpha = 95.28°$

Layer 2 PbS; space group $C2/m$
$(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (\mathbf{a}_{21}, \mathbf{a}_{22}, \mathbf{a}_{13})$, **a** axis unique
Unit cell: 5.800, 5.881, 11.670 Å, $\alpha = 95.28°$

Table 9.1). The structure and symmetry properties of LANBS are described by Meerschaut, Rabu & Rouxel (1989), Wiegers *et al.* (1990) and van Smaalen (1991); those of PBTIS are described by van Smaalen, Meetsma, Wiegers & de Boer (1991). The same test compounds were used in (Ref. I). The structure of LANBS is given in Figure 9.1.

Symmetry

In the following arguments, we assume that the symmetry is known. Note that, if there is any doubt about the four-dimensional symmetry, it is trivial to try out all possible symmetries (as is being done for three-dimensional structures having space-group ambiguities). With the modern computational facilities available, a complete analysis is a matter of a few minutes.

9.2 Determination of the two substructures

Reflection data and space groups

The reflections $HKL0$ and $0KLM$ represent the main reflections of layers 1 and 2, respectively. No further restrictions apply to the settings. In order to be able to use all

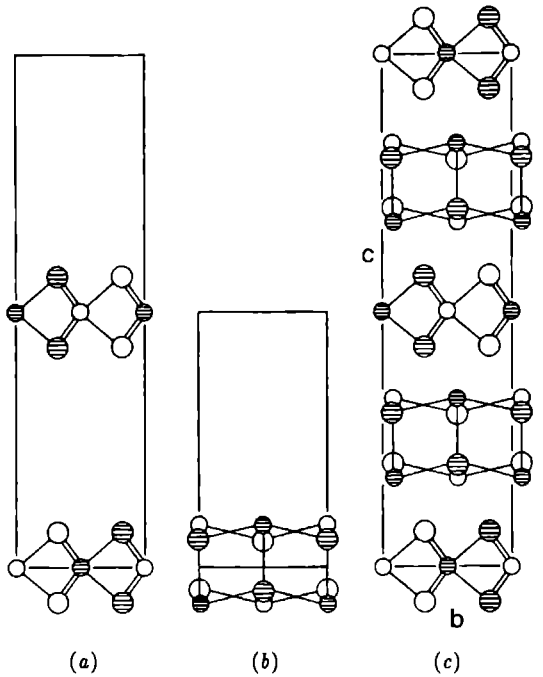


Figure 9.1. The structure of LANBS projected along the incommensurate a axes Large circles are sulphur and small open or black circles are metal atoms Left the NbS_2 basic structure as found for layer 1 Middle the LaS basic structure as found for layer 2, unshifted Right layer 1 and 2 combined, layer 2 has been shifted to the correct relative position

modern computer programs for crystallographic calculations, we use the matrices B_ν for the transformation to a conventional space-group setting

LANBS For NbS_2,

$$B_1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix},$$

for LaS,

$$B_2 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

For layer 1, $HKL0$ is transformed to $hkl = HKL$. For layer 2, $0KLM$ is transformed to $hkl = MK\frac{1}{2}L$ with a half-length **c** axis. Note that layer 1 is a 'zig-zag' double layer and layer 2 is a 'pure' translational double layer (see Figure 9.1).

Unit-cell contents

The approximate composition of the structure is known from chemical analysis and the volumes of the unit cells of the basic structures are known from the diffraction pattern (otherwise we could not index the diffraction pattern); this information is usually sufficient to determine the contents of each of the two unit cells. Note that the ratio $|\mathbf{a}_{11}| : |\mathbf{a}_{12}|$ determines the nonstochiometricity of the composition.

LANBS. The unit cell of layer 1 appears to contain 'approximately' one independent Nb atom. As in conventional structure analysis, it is assumed that in this case the cell contains precisely one Nb atom (whether or not some slight occupancy modulation exists is irrelevant at this stage of the analysis).

Note. It is expected that an error in the composition is not of great importance, because the heavy atom(s) will dominate and have sufficient scattering power to allow the calculation of sufficiently accurate phases for steps (iii) and (iv) of the procedure.

Patterson interpretation

For each layer, reflection data (hkl), symmetry information and cell contents are written to data files to be used in the structure analysis using conventional techniques (see Section 9.5). After the basic structure of the first layer has been solved, the basic structure of the second layer is solved likewise.

For each layer, the atomic parameters for all atoms of the layer and a list (file) of calculated structure factors are tabulated for use in steps (iii) and (iv). The conventional R value is expected to be in the range $R = 0.15$ to 0.30.

LANBS. Layer 1, $R = 0.18$; Layer 2, $R = 0.15$.

Notes

(1) For very simple inorganic basic structures, the present Fourier refinement gives sufficiently accurate results and (at this stage) we do not consider further refinement of the

basic structures to be of importance for the performance of steps (iii) and (iv). If, however, more complicated structures are being analyzed, one could easily call a least-squares program for a block-diagonal structure refinement.

(2) For complicated structures, the present automatic Patterson interpretation may fail for one or both basic structures. In this case, users are advised to solve the structure(s) using their own experience and/or other available programs and techniques and, subsequently, to supply the atomic parameters in a restart of the program *MISFIT* (see Section 9.5).

The role of the common projection reflections $0KL0$

The reflection data for each of the layers have the $0KL0$ projection reflections in common. The (projected) atomic positions of both layers contribute to the Bragg scattering: the structure factor for a $0KL0$ reflection is the weighted sum of the structure factors of the individual layers. Therefore, the corresponding structure-factor magnitude of one layer is not known from experiment. The correct expression for the $0KL0$ structure factor is given in Section 9.3. Here, we are concerned with the value of the corresponding structure factors to be used for the calculation of the two Patterson syntheses.

Simple statistical considerations lead to the following conclusions. (1) A weak $0KL0$ reflection could result from strong contributions of the two layers with opposite phases, but it is more likely that both contributions are weak. (2) A strong $0KL0$ reflection could result from a very strong contribution and a weak contribution, but it is more likely that both contributions are medium to strong. Therefore, it is as incorrect to use the observed structure factors as it is to substitute zero values. We have considered using the expectation values for the common projection reflections, which can be derived from the relative scattering powers of the individual layers:

$$(p^2)_\nu = \sum_\nu Z^2 \left(\sum_1 Z^2 + \sum_2 Z^2 \right)^{-1} ,$$

where $\sum_\nu$ denotes summation over all atoms in layer ν per unit volume. This leads to an equal chance of over- or underestimation of the Patterson coefficient. It is better to use smaller values because overestimation of the 'observed' structure factors enhances the contributions of the (projected) atomic positions of the other layer and therefore gives rise to false peaks in the Patterson, which may do more harm than underestimation of the Patterson coefficients.

In Table 9.2, we compare the relative peak heights of the weakest Patterson vectors, *i.e.*

S–S for each of the two layers of the test structures LANBS and PBTIS, for three cases, using $I_o = 0$, $I_o = 0.25I(0KL0)$ and $I_o = I(0KL0)$, where $I(0KL0) = |F(0KL0)|^2$ and I_o is the value of the Patterson coefficient to be substituted for the corresponding common reflections. In all cases, the metal and S atoms are easily located, but the S–S peaks are better defined when the intermediate I_o values are used. Note that, in the Patterson of the light TiS_2 structure, the S–S peak is clearly above background but the Patterson function is strongly influenced by too large $I(0KL0)$ magnitudes arising from the heavy PbS layer.

As a result of the simple tests described, for the time being we have instructed the program *MISFIT* to use $0.5\,|F(0KL0)|$ as a substitute for the observed structure factor of the corresponding projection reflection of each layer.

Note. For larger structures, the projection reflections generally become relatively less important. Nevertheless, in case one encounters problems in the solution of the structure of one of the individual layers, the value of the structure factors of the common projection reflections can be estimated more accurately by using the calculated structure factors of the corresponding reflections of the other known layer. This is not done automatically by the program *MISFIT*.†

After the solution of the basic structure of a layer, the atomic parameters have to be transformed back to express the atomic positions as fractional coordinates in the original axial system of the composite structure by B_ν [(9.1)]. If the origin for the definition of the four-dimensional symmetry elements differs from the origin setting used in the (conventional!) three-dimensional space group, one must also shift the atomic parameters of each substructure to be consistent with the proper setting of the four-dimensional superspace group. This shift vector is denoted $\mathbf{s}_\nu$.

Notes

(1) $F_1(HKL0)$ and $F_2(0KLM)$ have been calculated using the standard three-dimensional procedures; the back transformation to the four-dimensional $HKLM$ description does not effect the (complex) value of the structure factor. If, however, a symmetry shift $\mathbf{s}_\nu$ is required, then the structure factor has to be multiplied by the corresponding phase factor

$$\exp[2\pi i(Hs_{11} + Ks_{12} + Ls_{13})]$$

†We would be interested to receive notice of possible misfit compounds for which this could be of importance to the solution of the structure.

Table 9.2. Comparison of Patterson peak heights in the test structures

The relative values of the peaks are given for three cases of I_o (substituted value of the Patterson coefficients for common projection reflections; see text). Underscored false peaks are larger than an S–S peak. p^2 is the relative scattering power of the substructure. Origin: peak height set equal to $\sum_\nu Z^2$ of the substructure.

(a) LANBS

Interatomic vectors	$I_o(0KL0) = 0$	$I_o = \frac{1}{4}I(0KL0)$	$I_o = I(0KL0)$
Layer 1, NbS_2, $p^2 = 0.35$			
Nb–Nb	2193 = origin	2193 = origin	2193 = origin
Nb–S	446	429	380
S–S	154	165	181
False peaks	160 126 ...	121 114 ...	233 188 156 ...
Layer 2, LaS, $p^2 = 0.65$			
Origin	3505	3505	3505
La–La	1568	1434	1323
La–S	950 906	865 859	769 650
S–S	159	137	88
False peaks	169 158 ...	166 120 ...	497 247 199 ...

(b) PBTIS

Interatomic vectors	$I_o(0KL0) = 0$	$I_o = \frac{1}{4}I(0KL0)$	$I_o = I(0KL0)$
Layer 1, TiS_2, $p^2 = 0.11$			
Ti–Ti	996 = origin	996 = origin	996 = origin
Ti–S	624	551	409
S–S	207	175	129
False peaks	44 ...	75 ...	366 167 163 ...
Layer 2, PbS, $p^2 = 0.89$			
Origin	6980	6980	6980
Pb-Pb	3306	3293	3185
Pb–S	991 891	967 849	903 741
S–S	207	194	313
False peaks	208 164 ...	197 193 ...	404 282 ...

or

$$\exp[2\pi i(Ms_{21} + Ks_{22} + Ls_{23})],$$

where $s_{\nu i}$ is the ith component of $\mathbf{s}_\nu$.

(2) The components s_{22} and s_{23} of the shift vector for layer 2 are irrelevant, as they will be redetermined as described in Section 9.3.

9.3 Shift function

Once each of the two layers has been solved, they have to be positioned relative to each other. Shifts parallel to the incommensurate axis ($\mathbf{a}_{11} \parallel \mathbf{a}_{21}$) are of no physical relevance. Such shifts redefine the mathematical description of the atomic positions and the phases of the atomic modulation functions but do not affect the distribution of interatomic distances. So we only consider the possible shifts along other directions.

Shifts in these directions are restricted to shifts between permissible origins in the original three-dimensional symmetry descriptions of the individual layers. Thus, the reflections $0KL0$ contain the information to position the layers. The structure factors of the $0KL0$ reflections are given by

$$F(0KL0) = V_1^{-1}[F_1(0KL0)] + V_2^{-1}[F_2(0KL0)] \tag{9.2}$$

(van Smaalen, 1992), where V_ν is the volume of the unit cell of the basic structure of layer ν and $F_\nu(0KL0)$ is the calculated structure factor of layer ν (electrons per unit cell V_ν).

We now keep the first layer fixed and shift the second layer over a two-dimensional vector $\mathbf{t} = (t_2, t_3)$. The structure factors for the $0KL0$ reflections calculated for layer 2, denoted F_2', are then to be multiplied by the phase factor $\exp[2\pi i(Kt_2 + Lt_3)]$ before substitution in (9.2).

The vector $\mathbf{t}$ minimizes the disagreement or maximizes the correlation between $F_{\rm obs}$ and $F_{\rm calc}$ for the $0KL0$ reflections. Usually, conventional R or $R2$ minimization or least-squares procedures are employed.

It has been argued that there are great similarities between the various forms of translation functions (Beurskens, Gould, Bruins Slot & Bosman, 1987) and, because the two fragments (*i.e.* layer 1 and layer 2) constitute the complete structure, we do not have to be very subtle about the subtraction of origin and intralayer vector contributions (as in small-fragment Patterson searches). We have chosen to maximize the simple correlation

function

$$T(\mathbf{t}) = \sum_{0KL0} F_{\mathrm{obs}}^2(0KL0)\left\{V_1^{-1}[F_1(0KL0)] + V_2^{-1}[F_2'(0KL0)]\exp[2\pi i(Kt_2 + Lt_3)]\right\}^2 . \tag{9.3}$$

Note that for conventional Patterson searches sharpening is advised but, in view of the uncertainty of the calculated structure factor (arising from incomplete refinement of the basic structures and ignoring the modulation effects so far), we prefer to use no sharpening or (subject to future modifications) only a slight sharpening.

If nothing is 'wrong' with the structure determination of either layer then the maximum of the function $T(\mathbf{t})$ is found for the correct shift vector $\mathbf{t}$.

LANBS. The shift vector found is $\mathbf{t} = (0.08, 0.25)$. As can be seen from Figure 9.1, the LaS layer must be shifted by $\Delta z = \frac{1}{4}\mathbf{a}_{23}$, which corresponds to $\Delta z = \frac{1}{2}\mathbf{c}$ in the B_2-transformed setting, which reflects the presence of two mirror planes (at $z = 0$ and $z = \frac{1}{2}$) in the three-dimensional basic structure. This component of the shift vector $\mathbf{t}$ is rather trivial, as otherwise the layers would severely overlap. It is seen also from Figure 9.1 that the LaS layer is shifted a little bit along the $\mathbf{a}_{22}$ axis, which reflects the fact that in both layers the $\mathbf{b}$ axis is a polar axis (a twofold rotation axis). The magnitude of this shift is found to be $\Delta y = 0.08$. This component is not trivial as it is essential to achieve correct physical contact (bond distances and angles) between the layers.

Enantiomer fixation?

If the individual layers have not been refined (as we have assumed here) prior to the determination of the shift vector for layer 2, and if both basic structures are noncentrosymmetric, then the absolute structures of the layers are not known and we have a fifty-fifty chance of success or failure. So we must also invert one of the layers and repeat the shift calculations for this case; if we find a higher maximum in the shift function $T(\mathbf{t})$, then we have to accept the inverted layer as being correct.

LANBS. In this example, the LaS structure is described in a noncentrosymmetric space group, but the LaS structure is almost perfectly centrosymmetric and consequently the enantiomer test does not show a significant difference for the two possibilities: the slight observed difference in the $T(\mathbf{t})$ maxima can easily be accounted for by small errors in the structural parameters and neglect of anomalous scattering. Either choice can be used as a starting point for further analysis.

9.4 Direct methods

The phases of the main reflections of the two layers can be calculated from the known structural parameters (see Section 9.2). For layer 2, we may have to apply the structural inversion (enantiomer change, phases φ replaced by $-\varphi$) and then apply the layer shift as a phase shift. Thus, the outcome of the foregoing section is that we now have available the structure-factor magnitudes and phases of the main reflections $HKL0$ and $0KLM$.

The modified Sayre equation to be used (Ref. I) is

$$\varphi[F(HKLM)] = \varphi\left\{\sum_{K'L'}[F(H, K-K', L-L', 0)F(0K'L'M)]\right\}, \qquad (9.4)$$

with $H \neq 0$ and $M \neq 0$. All main reflections [right-hand side of (9.4)] are used to calculate the phases of all observed satellite reflections.

Notes

(1) Refinement by direct methods of the main ($HKL0$ and $0KLM$) reflections is useless: if better phases are necessary, the individual three-dimensional basic structures can be refined by conventional least-squares methods.

(2) The $0KL0$ reflections do not participate in the Sayre equation [(9.4)] as they do not contribute to the satellite phases.

(3) Unobserved or very weak satellite reflections (intensity less than 3σ) will not be phased but all others will be, as well as the weak reflections; there is nothing to be gained by leaving those out, as in standard three-dimensional direct methods.

(4) The full Sayre equation is much more powerful than the conventional tangent formula applied to a limited number of strong normalized structure factors. Therefore, conventional normalization is not useful.

(5) The application of the Sayre equation to one set of phases does not require much computer time. Because many starting phases are known (all main reflections), there is no need for random phases or multisolution techniques.

9.5 Computer program MISFIT

The procedure described in this paper is implemented in the program *MISFIT*. It is a new entry in the *DIRDIF* system (Beurskens *et al.*, 1992). In this system, technically independent programs communicate with one another by means of control and data files.

The first program to be executed reads the instruction given by the user and, if it contains the keyword MISFIT, passes control on to the program *MISFIT*.

MISFIT reads a user-prepared crystal data file (CONDA) and writes a history file (DDLOG) to determine what is to be done next.

At the first call, *MISFIT* reads the first part of the CONDA file, which contains the crystal data for layer 1. If this data part does not contain atomic parameters, *MISFIT* prepares various data and control files for the automatic execution of all that is needed to solve the basic structure of layer 1 and then returns control to the *DIRDIF* system.

Major programs to be called are *FOUR*, *PATTY* and *PHASEX*. *FOUR* and *PATTY* are used for the calculation of the Patterson synthesis and its automatic heavy-atom interpretation (Admiraal, Behm, Smykalla & Beurskens, 1992). The resulting atomic parameters are passed on to program *PHASEX* for phase expansion and phase refinement using direct methods on difference structure factors (Beurskens & Smykalla, 1991). This is followed by *FOUR*, peak interpretation and automatic *PHASEX*/*FOUR* recycling. In case the atomic parameters are given by the user as part of the CONDA file, the solution of the structure is bypassed, but control is still given to the system for the preparation of various data and control files.

After completion of the analysis of layer 1, control is returned to *MISFIT*. At this second call, structure factors for layer 1 are calculated and saved on a reflection data file for later use.

MISFIT then continues to read the second part of the CONDA file, which contains the crystal data for layer 2. This layer is solved as described above for layer 1.

After completion of the analysis of layer 2, control is returned to *MISFIT* again. At this third call, structure factors for layer 2 are calculated. At this stage, all data are available for the calculation of the shift function $T(\mathbf{t})$. The resulting shift vector $\mathbf{t}$ is used to shift the atomic parameters of layer 2, to modify the phases of the calculated structure factors of the $0KLM$ reflections and to calculate correct structure factors for the $0KL0$ reflections using (9.2).

LANBS. The conventional R value for the $0KL0$ reflections is $R = 0.13$

Finally, the third part of the CONDA file is read, which contains the full four-dimensional symmetry operators to be used for the application of the Sayre equation, *i.e.* to determine the phases of the satellite reflections.

The output reflection data file is in the format ready for use in the four-dimensional Fourier program of Petříček (1993).

Table 9.3. Test results for the two test structures

Averaged phase errors $\langle|\Delta\varphi|\rangle$ of the reflections obtained by the present procedure, as compared to the phases calculated from the refined (four-dimensional) composite structures. R and $\langle|\Delta\varphi|\rangle$ for the main reflections show the results of the three-dimensional structure solutions and the quality of the phases used as input to the tangent formula, while $\langle|\Delta\varphi|\rangle$ for the satellites shows the quality of the phases of these reflections as obtained by direct methods. R is the conventional R value for the unrefined structure. N_{ref} is the number of reflections.

		LANBS			PBTIS		
		N_{ref}	R	$\langle\|\Delta\varphi\|\rangle$	N_{ref}	R	$\langle\|\Delta\varphi\|\rangle$
Layer 1	$HKL0$	261	0.18	5.1	500	0.24	11.9
Layer 2	$0KLM$	393	0.15	11.9	1131	0.23	21.2
Common projection	$0KL0$	70	0.13	9.9	169	0.16	29.1
Satellites	$HKLM$	263		18.9	190		16.2
Ref. 1	$HKLM$	276		17.6*	190		5.6*

* Test results, given in Ref. 1, obtained using phases from the refined structure as input to the tangent formula.

Test results

Table 9.3 gives the results for the two test structures, *i.e.* R values and average phase errors after the structure analyses of the basic structures, the calculation of the shift functions and the determination of the phases of the satellites by direct methods. These test results show that the satellite phases are well determined. The average phase errors are just slightly larger than in previous results (Ref. I). There is no doubt that the four-dimensional Fourier synthesis will show the modulations of atoms. Sections from some similar Fourier calculations were presented in Ref. I.

LANBS. The complete analysis was performed in 5 minutes on a 80486 PC.

Program symmetry considerations

All symmetry information is in principle available from the four-dimensional symmetry operations, given by the user in the CONDA file. The reflection transformation matrices B_ν, however, are provided and applied to prevent cumbersome settings for the basic structures. The corresponding three-dimensional symmetry can be obtained from the four-dimensional operations. But here is a software problem: *DIRDIF* (used for Patterson interpretation, *etc.*) requires the space-group symbol as input. Instead of writing a complicated routine to derive the space-group symbols from the symmetry operations, we ask the user to supply

the proper space-group symbols and the possible origin-shift vectors $\mathbf{s}_\nu$. Thus, the handling of symmetry is open for future updates of the program *MISFIT*.

Availability

All *DIRDIF* programs are written in standard Fortran77 and are highly computer independent. The system, *MISFIT* included, is available from one of the authors (PTB) on request.

Generalization

Column composite structures and higher-dimensional layer composite structures can be handled with essentially identical procedures. Implementation in *MISFIT* will follow in due course.

Acknowledgements

Part of this work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO).

References

ADMIRAAL, G., BEHM, H., SMYKALLA, C. & BEURSKENS, P. T. (1992). *Z. Kristallogr.* Suppl. No. 6, p. 522.

BEURSKENS, P. T., ADMIRAAL, G., BEURSKENS, G., BOSMAN, W. P., GARCIA-GRANDA, S., GOULD, R. O., SMITS, J. M. M. & SMYKALLA, C. (1992). *The DIRDIF Program System.* Technical Report, Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.

BEURSKENS, P. T., GOULD, R. O., BRUINS SLOT, H. J. & BOSMAN, W. P. (1987). *Z. Kristallogr.* **179**, 127–159.

BEURSKENS, P. T. & SMYKALLA, C. (1991). *Direct Methods of Solving Crystal Structures*, edited by H. Schenk, pp. 281–290. New York: Plenum Press.

FAN H.-F., SMAALEN, S. VAN, LAM, E. J. W. & BEURSKENS, P. T. (1993). *Acta Cryst.* A**49**, 704–708.

FU Z.-Q. & FAN H.-F. (1994). *J. Appl. Cryst.* **27**, 124–127.

HAO, Q., LIU, Y.-W. & FAN, H.-F. (1987). *Acta Cryst.* A**43**, 820–824.

JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* A**36**, 408–415.

MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1989). *J. Solid State Chem.* **78**, 35–45.

PETŘÍČEK V. (1993). *Computing System JANA*93. Institute of physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic.

SMAALEN, S. VAN (1991). *J. Phys. Condens. Matter*, **3**, 1247–1263.

SMAALEN, S. VAN (1992). *Mater. Sci. Forum*, **100&101**, 173 -222.

SMAALEN, S. VAN, MEETSMA, A., WIEGERS, G. A. & BOER, J. L. DE (1991). *Acta Cryst.* B**47**, 314–325.

WIEGERS, G. A. & MEERSCHAUT, A. (1992). *Mater. Sci. Forum*, **100&101**, 101–172.

WIEGERS, G. A., MEETSMA, A., HAANGE, R. J., SMAALEN, S. VAN, BOER, J. L. DE, MEERSCHAUT, A., RABU, P. & ROUXEL, J. (1990). *Acta Cryst.* B**46**, 324–332.

Summary

In contrast to ordinary crystals, aperiodic crystals, such as incommensurately modulated crystals and misfit layer compounds, do not have three-dimensional translational symmetry. However, long-range order does exist in these crystals, as is obvious from the appearance of Bragg peaks in their diffraction patterns. In fact, aperiodic crystals can be considered as embedded in a supercrystal that is lattice periodic in a four- or higher-dimensional superspace. For conventional crystals, all Bragg peaks can be associated with the nodes of a three-dimensional reciprocal lattice. For aperiodic crystals, this is no longer true. Diffraction patterns of incommensurately modulated crystals and misfit layer compounds contain two types of reflections: main reflections and satellite reflections. The satellite reflections do not belong to the same three-dimensional reciprocal lattice(s) as the main reflections. Because of the different origin of their X-ray diffraction intensities, it is expected that the statistical behavior of satellite reflections is different from that of main reflections.

Today, many conventional crystal structures can be solved by direct-methods procedures employing statistical relations between the phases of the structure factors. However, a straightforward application of these procedures to aperiodic crystals is impossible because the statistical behavior of the X-ray diffraction intensities of these crystals is unknown. Or better: was unknown!

In this thesis, the extension of the statistical methods underlying the various direct-methods procedures to incommensurately modulated crystals and misfit layer compounds, that can be considered as lattice-periodic structures in four-dimensional superspace, has been initiated. In particular, a statistical background was developed for the definition of normalized structure factors of incommensurately modulated crystals.

In Chapters 2 and 3 of this thesis, expressions were derived for the average X-ray diffraction intensities of incommensurately modulated crystals. The parameters describing the displacive modulations and occupancy-factor modulations of the individual atoms were replaced by overall modulation parameters. The expressions for the average intensities lead to practical definitions of normalized structure factors, which could be used to estimate normalized structure-factor amplitudes from the experimental X-ray diffraction data.

In Chapter 4 of this thesis, analytical expressions were derived for the probability density functions (p.d.f.s) of structure factors of incommensurately modulated crystals. These p.d.f.s lead to a theoretical definition of normalized structure factors. In a first-order approximation, the p.d.f.s of the newly defined normalized structure-factor amplitudes proved to be of the same functional form for main reflections and for satellites and, in addition, these functions were identical to similar p.d.f.s of normalized structure-factor

amplitudes of conventional crystals, in the same approximation.

In Chapters 5 and 6 of this thesis, the newly defined normalized structure factors were tested with regards to their applicability in direct-methods procedures for phase determination. In Chapter 5, the reliability of the triplet-phase relation and the tangent formula were examined. In Chapter 6, the newly defined normalized structure factors were used in a direct-methods procedure to solve the structure of (perylene)$Co(mnt)_2(CH_2Cl_2)_{0.5}$, an unknown incommensurately displacively modulated structure. These tests showed that the newly defined normalized structure factors can be used successfully in direct-methods procedures.

In Chapters 7 and 8 of this thesis, the extension of direct methods to misfit layer compounds has been investigated. In Chapter 7, a modified version of the Sayre equation was used to estimate phases of satellite reflections from the known amplitudes and phases of the main reflections. In Chapter 8, the procedure developed in Chapter 7 was extended to also estimate the amplitudes of the satellite reflections. Satisfactory results were obtained.

In Chapter 9 of this thesis, it is shown that classical Patterson methods can be used to solve the individual (three-dimensional) substructures of misfit layer compounds. A shift function is then used to bring the individual layers to a common origin in four-dimensional space. Direct methods are then used to obtain the phases of the satellite reflections. This procedure is performed fully automatically by the program system *DIRDIF*, where the program *MISFIT* controls all necessary calculations.

Samenvatting

In tegenstelling tot gewone kristallen, hebben aperiodieke kristallen, zoals incommensurabel gemoduleerde kristallen en misfit-lagen verbindingen, geen drie-dimensionale roostertranslatiesymmetrie. In deze kristallen komt echter wel degelijk een zekere mate van langeafstands-ordening voor. Dit blijkt duidelijk uit de aanwezigheid van Bragg pieken in de diffractiepatronen van deze kristallen. In feite kan een aperiodiek kristal beschouwd worden als ingesloten in een superkristal dat translatieperiodiek is in een ruimte met meer dan drie dimensies, de superruimte. Voor gewone kristallen kunnen de Bragg pieken geassocieerd worden met de knooppunten van het drie-dimensionale reciproke rooster. Voor aperiodieke kristallen is dit niet meer mogelijk. Diffractiepatronen van incommensurabel gemoduleerde kristallen en misfit-lagen verbindingen bevatten twee soorten reflecties: hoofdreflecties en satelliet reflecties. De satelliet reflecties behoren niet tot hetzelfde (dezelfde) drie-dimensionale reciproke rooster(s) als de hoofdreflecties. Omdat de röntgendiffractie intensiteiten van deze twee typen reflecties een verschillende oorsprong hebben, mag men verwachten dat het statistische gedrag van de satelliet reflecties verschilt van dat van de hoofdreflecties.

Tegenwoordig wordt van veel gewone kristallen de structuur bepaald door middel van directe-methoden procedures die gebruik maken van statistische relaties tussen de fasen van de structuurfactoren. Het is echter onmogelijk om de bestaande methoden voor structuurbepaling rechtstreeks te gebruiken voor aperiodieke kristallen omdat voor deze kristallen het statistische gedrag van de intensiteiten van de verstrooide röntgenstralen onbekend is. Of beter: onbekend was!

In dit proefschrift wordt een begin gemaakt met de uitbreiding van de statistische methoden, die de grondslag vormen voor de verschillende directe-methoden procedures, naar aperiodieke kristallen. Hierbij beperken we ons tot incommensurabel gemoduleerde kristallen en misfit-lagen verbindingen, die opgevat kunnen worden als translatieperiodieke structuren in een vier-dimensionale superruimte.

In de hoofdstukken 2 en 3 van dit proefschrift worden, voor incommensurabel gemoduleerde kristallen, uitdrukkingen afgeleid voor de gemiddelde röntgendiffractie intensiteiten van de hoofd- en satelliet reflecties. De atomaire parameters van de verplaatsingsmodulatie en de bezettingsfactormodulatie zijn hierbij vervangen door gemiddelde modulatie parameters. De uitdrukkingen voor de gemiddelde intensiteit resulteren in praktijk gerichte definities voor genormaliseerde structuurfactoren. Deze definities kunnen gebruikt worden voor het berekenen van de genormaliseerde structuurfactoramplituden uit de waargenomen reflectie intensiteiten.

In hoofdstuk 4 van dit proefschrift worden analytische uitdrukkingen afgeleid voor de waarschijnlijkheidsdichtheidsfuncties voor structuurfactoren van incommensurabel gemoduleerde kristallen. Deze waarschijnlijkheidsdichtheidsfuncties leiden tot een theoretische definitie van genormaliseerde structuurfactoren. In eerste benadering zijn de waarschijnlijkheidsdichtheidsfuncties van de zojuist gedefinieerde genormaliseerde structuurfactoramplituden voor zowel hoofdreflecties als satelliet reflecties identiek. Bovendien hebben deze waarschijnlijkheidsdichtheidsfuncties dezelfde functionele gedaante als overeenkomstige waarschijnlijkheidsdichtheidsfuncties voor genormaliseerde structuurfactoramplituden van gewone kristallen, uitgaande van dezelfde benadering.

In de hoofdstukken 5 en 6 van dit proefschrift worden de zojuist gedefinieerde genormaliseerde structuurfactoren getest met betrekking tot hun bruikbaarheid ten behoeve van directe methoden voor het bepalen van de fasen van de structuurfactoren. In hoofdstuk 5, wordt de betrouwbaarheid van de triplet-fase relatie en de tangent formule bestudeerd. In hoofdstuk 6 worden de zojuist gedefinieerde genormaliseerde structuurfactoren gebruikt in een directe-methoden procedure voor het bepalen van de incommensurabel gemoduleerde structuur van (peryleen)$Co(mnt)_2(CH_2Cl_2)_{0.5}$, een onbekende structuur met een verplaatsingsmodulatie. Deze tests tonen aan dat de zojuist gedefinieerde genormaliseerde structuurfactoren met succes gebruikt kunnen worden in direct-methoden procedures.

In de hoofdstukken 7 en 8 wordt de uitbreiding van de direct methoden naar misfit-lagen verbindingen onderzocht. In hoofdstuk 7, wordt een gemodificeerde versie van de Sayre vergelijking gebruikt om, met behulp van de bekende fasen en amplituden van de hoofdreflecties, de fasen van de satelliet reflecties te schatten. In hoofdstuk 8 worden ook de amplituden van de satelliet reflecties geschat. Dit vereist een uitbreiding van de procedure die in hoofdstuk 7 ontwikkeld werd. De verkregen resultaten blijken bevredigend.

In hoofdstuk 9 van dit proefschrift wordt aangetoond dat klassieke Patterson methoden gebruikt kunnen worden om de gemiddelde (drie-dimensionale) structuur van de individuele lagen van misfit-lagen verbindingen te bepalen. Hierna wordt een translatiefunctie gebruikt om in de vier-dimensionale superruimte de beide lagen naar een gemeenschappelijke oorsprong te brengen. Vervolgens wordt de directe-methoden procedure uit hoofdstuk 7 gebruikt om de fasen van de satelliet reflecties te schatten. Deze gehele procedure wordt volledig automatisch uitgevoerd door het programma systeem *DIRDIF*, waarbij het programma *MISFIT* toezicht houdt op alle benodigde berekeningen.

Curriculum vitae

Erwin Jacobus Wilhelmus Lam werd geboren op 10 september 1960 te Hilversum. Na het behalen van het VWO-B diploma in 1978 aan het Alberdingk Thijm College aldaar, werd in datzelfde jaar een aanvang gemaakt met de studie natuurkunde aan de Rijksuniversiteit Utrecht.

In september 1982 werd het kandidaatsexamen natuurkunde, met bijvak sterrenkunde, behaald. Het doctoraalexamen experimentele natuurkunde, met groot bijvak kernfysica, werd vervolgens afgelegd in september 1987. Het practische werk bij de vakgroep Kernfysica betrof het ontwikkelen van een automatisch computerprogramma ten behoeve van het berekenen van vormfactoren voor verstrooiing van electronen aan lichte atoomkernen. Tevens werd tijdens de doctoraal fase van de studie practisch werk verricht bij de vakgroep Atoom en Molecuul Fysica. Hier werd, ten behoeve van het research practicum, een Stark-modulatie spectrometer gebouwd.

Van september 1987 tot en met oktober 1988 werd de militaire dienstplicht vervuld bij de Koninklijke Landmacht.

Vanaf 1 november 1988 tot 1 november 1992 was hij, in dienst van NWO/SON, als onderzoeker-in-opleiding werkzaam bij de afdeling Kristallografie van de vakgroep Algemene en Anorganische Chemie van de Katholieke Universiteit Nijmegen, alwaar het in dit proefschrift beschreven promotie-onderzoek werd verricht onder leiding van Prof. Dr. P. T. Beurskens. Dit onderzoek werd afgesloten in november 1994. In het kader van de met deze aanstelling samenhangende onderwijstaak verzorgde hij tevens werkcolleges 'Kristalchemie' en 'Inleiding Structuur' voor eerstejaars studenten.

Financiële steun van de NWO/SON maakte het mogelijk om in de periode van het promotie-onderzoek deel te nemen aan de 'Sixteenth Course of the International School of Crystallography', te Erice, Italië (1990); aan de 'International Workshop on Methods of Structural Analysis of Modulated Structures and Quasicrystals', te Lekeitio, Spanje (1991) en aan de 'Fourteenth European Crystallographic Meeting (ECM14)', te Enschede, Nederland (1992).

Tevens werd in het kader van het onderwijsprogramma voor AIO/OIO studenten deel genomen aan de cursussen 'The Phase Problem of X-ray Crystallography' van Professor H. A. Hauptman, Amsterdam, 1988; 'Kristalstructuurbepalingsmethoden en diffractiefysica (II)', Utrecht, 1989; 'Tensoriële eigenschappen van kristallen (waaronder kristaloptica) en electronenmicroscopie', Delft, 1990 en aan de cursus 'Kristalgroei en oppervlakken', Utrecht, 1991. Voor de cursus te Delft werd subsidie ontvangen van de SON.

(*OK* en *RdG*)